

Short Communication

Cathodic electrochemiluminescence performance of all-inorganic perovskite CsPbBr₃ nanocrystals in an aqueous mediumHuaping Peng^{a,1}, Weihua Wu^{a,1}, Zhongnan Huang^a, Luyao Xu^a, Yilun Sheng^a, Haohua Deng^a, Xinghua Xia^b, Wei Chen^{a,*}^a School of Pharmacy, Fujian Medical University, Fuzhou 350004, Fujian Province, China^b State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210093, China

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ABSTRACT

We report cathodic electrochemiluminescence (ECL) from all-inorganic perovskite nanocrystals (NCs) in an aqueous medium. An electron transfer annihilation pathway was proposed for the all-inorganic perovskite CsPbBr₃ NCs with potassium peroxydisulfate (K₂S₂O₈) as coreactant. In addition to the greenish ECL emission with its excellent stability, this study might open a door to further applications of perovskite-based ECL probes.

1. Introduction

All-inorganic halide perovskite nanocrystals (CsPbX₃ NCs, X = Cl, Br, and I) are currently the focus of a considerable research effort owing to their unequivocally orthorhombic structure and superior photoluminescence (PL) emission compared with traditional NCs [1]. So far, research into MPbX₃ NCs and their applications have been mostly limited to photovoltaic and optoelectronic devices [2–5]. It is now important to study the properties of CsPbX₃ NCs more deeply and to explore their potential use in a wider range of applications

Electrochemiluminescence (ECL) is a light radiation generated by the energy relaxation of an excited species induced by electrochemistry [6]. ECL has been widely used due to its high sensitivity, near-zero background signal, easy controllability and flexibility [7]. Inspired by the excellent optoelectronic properties of CsPbX₃ NCs, it is of great interest to explore their ECL performance. However, research into the ECL behavior of CsPbX₃ NCs is still in its infancy. Wang et al. proposed a monochromatic and electrochemical switchable ECL from perovskite CsPbBr₃ NCs in dichloromethane with tri-n-propylamine (TPRA) as coreactant [8]. Zhu's group has developed efficient solid-state ECL systems based on high-quality CsPbX₃ NCs and CsPbX₃@SiO₂ NCs with ethyl acetate and 2-(dibutylamino)ethanol (DBAE) as coreactants, respectively [9,10]. In addition, a closed bipolar electrode using CsPbBr₃ NCs with stable ECL has been proposed for detection of H₂O₂ [11]. But all of the above ECL systems based on all-inorganic perovskite CsPbBr₃ NCs, even lead-free all-inorganic perovskite Cs₃Bi₂Br₉ NCs

[12], require organic solvents. This greatly limits their application, especially in bioanalysis. To overcome this problem, anodic ECL systems of all-inorganic CsPbX₃ NCs in aqueous solution have been proposed [13]. However, the main challenge for anodic ECL is the interference of compounds in real samples that could be oxidized on the electrode at high positive potentials. Cathodic ECL has many advantages, such as extending the number of possible ECL reactions, eliminating the oxidation products of luminophores, and removing the interference of compounds present in the sample [14]. Therefore, it is important to explore the cathodic ECL properties of all-inorganic perovskite CsPbX₃ NCs, and expand their areas of application.

Herein, we report high-performance cathodic ECL of CsPbX₃ NCs in a purely aqueous solution. This study not only enriches the fundamental research into the ECL mechanisms of all-inorganic lead-halide perovskites, but also extends their huge potential application in ECL biosensing and nanodevices.

2. Materials and methods

Cesium carbonate (Cs₂CO₃, 99.995%), oleic acid (OA, ≥99%), oleylamine (OLA, ≥98%), 1-octadecene (ODE, ≥95%) and lead(II) bromide (PbBr₂, 99.999%) were purchased from Sigma-Aldrich. Hexane, potassium peroxydisulfate (K₂S₂O₈), Na₂HPO₄, NaH₂PO₄ and KCl were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Other reagents and chemicals were of analytical reagent grade. Solutions were prepared with water purified by a Milli-Q

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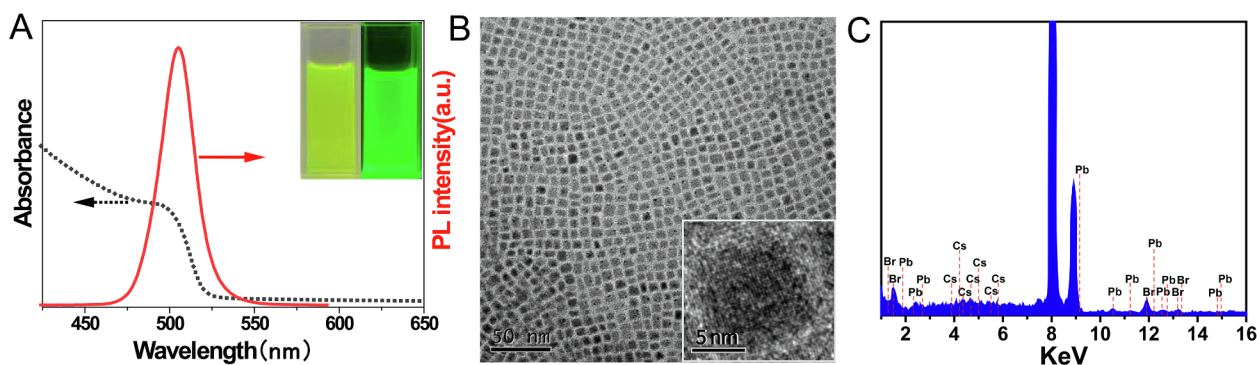


Fig. 1. (A) UV-vis absorbance and PL ($\lambda_{\text{ex}} = 260$ nm) spectra of the CsPbBr₃ NCs. The inset displays photos of CsPbBr₃ NCs under visible light (left) and 365 nm UV light (right). (B) TEM image of CsPbBr₃ NCs. The inset shows the HRTEM image of a single NC. (C) EDX pattern of CsPbBr₃ NCs.

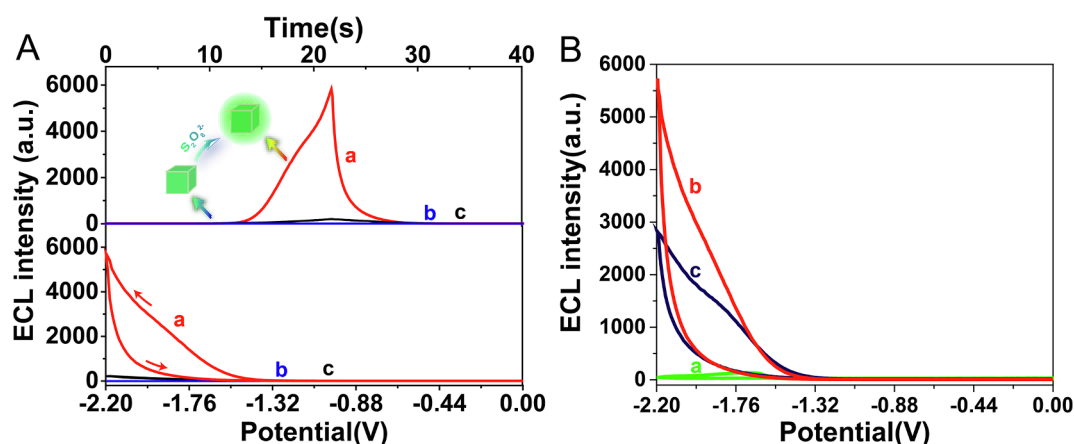


Fig. 2. (A) ECL-time curves (top) and ECL-potential-resolved curves (bottom) of the CsPbBr₃ NCs|GCE in 0.1 M pH 7.4 PBS containing (a) 0.1 M K₂S₂O₈ and (b) 0.1 M pH 7.4 PBS; (c) ECL curves of bare GCE in 0.1 M pH 7.4 PBS containing 0.1 M K₂S₂O₈. Scan rate, 0.1 V/s. (B) Potential-resolved ECL of (a) CH₃NH₃PbBr₃ NCs|GCE and (b) CsPbBr₃ NCs|GCE in 0.1 M pH 7.4 PBS containing 0.1 M K₂S₂O₈; (c) potential-resolved ECL of the CH₃NH₃PbBr₃ NCs|GCE in dichloromethane containing 0.1 M TBAPF₆ and 5 mM BPO.

purification system (Millipore, USA).

High-resolution transmission electron microscopy (HRTEM) images were collected with a JEM-2100 TEM instrument (JEOL, Japan). An energy-dispersive X-ray spectrometer (EDS) fitted to a transmission electron microscope operating in a nanoprobe mode was used for elemental analysis. The photoluminescence spectrum and the absorption spectra were recorded with a Cary Eclipse fluorescence spectrophotometer (Agilent, USA) and a Hitachi UV-2450 spectrophotometer (Shimadzu, Japan). The electrogenerated chemiluminescence (ECL) signals were captured by a MPI-E multifunctional chemiluminescence analyzer (Xienan Rimax Electronics Co. Ltd, China) with a three-electrode system where a modified glassy carbon electrode (GCE) was used as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. The photomultiplier tube (PMT) was biased at 700 V in the experiments. Differential pulse voltammetry (DPV) was recorded with a CHI660C electrochemical analyzer (Shanghai, China).

CsPbBr₃ NCs were prepared according to a method reported previously [15]. First, Cs oleate was prepared. 0.407 g Cs₂CO₃, 20 mL ODE and 1.25 mL OA were put into a 50 mL three-necked flask under vacuum, dried for 1 h at 120 °C, and then heated under N₂ atmosphere to 150 °C until all the Cs₂CO₃ had reacted. Then, 0.138 g PbBr₂, 10 mL dried ODE, 1 mL dried OA and OLA were put in a 25 mL three-necked flask, and heated under N₂ atmosphere to 160 °C until all the PbBr₂ had reacted. 0.8 mL Cs-oleate solution was quickly injected into the mixture, and 5 s later, the reaction mixture was cooled using ice-water. The resulting crude CsPbBr₃ NCs were separated by centrifuging at 12000 rpm, and then re-dispersed in 16 mL hexane. Finally, the

solution was determined to have a concentration of 25 mg·mL⁻¹.

CH₃NH₃PbBr₃ NCs were prepared according to the method of Huang et al [16]. First, 14.25 mL of HBr was added slowly into 15 mL methylamine at 0 °C with continuous stirring. After stirring for 1 h, the precipitate was obtained by rotary evaporation at 50 °C, followed by washing and centrifuging with diethyl ether three times, and the CH₃NH₃Br was obtained on drying the intermediate under vacuum. Next, CH₃NH₃Br and PbBr₂ (0.64 mmol), 500 μL OA, and 25 μL n-octylamine were dissolved in 5 mL N,N-dimethylformamide (DMF) and then slowly transferred into 30 mL of toluene under stirring. Two hours later, the final solution was centrifuged at 8000 rpm for 5 min; the resulting yellow precipitate was CH₃NH₃PbBr₃ NCs which was stored under dark conditions.

A glassy carbon electrode (GCE, 3 mm diameter, CH Instruments, Inc.) was wet polished carefully with 0.3 and 0.05 μm alumina slurry, followed by thorough washing with ultrapure water. The electrode was then successively sonicated in 1:1 nitric acid, ethanol and doubly distilled water, and then allowed to dry at room temperature. 5 μL of the CsPbBr₃ NC solution (0.6 mg·mL⁻¹) was then dripped onto the surface of the GCE and dried in air at room temperature. The modified electrode was denoted as CsPbBr₃ NCs|GCE.

3. Results and discussion

We prepared CsPbBr₃ NCs by the hot-injection method [15]. The CsPbBr₃ NCs displayed a sharp PL emission peak and an obvious excitonic peak at almost the same wavelength (around 500 nm), with a narrow full width at half-maximum (FWHM) value of 21 nm (Fig. 1A).

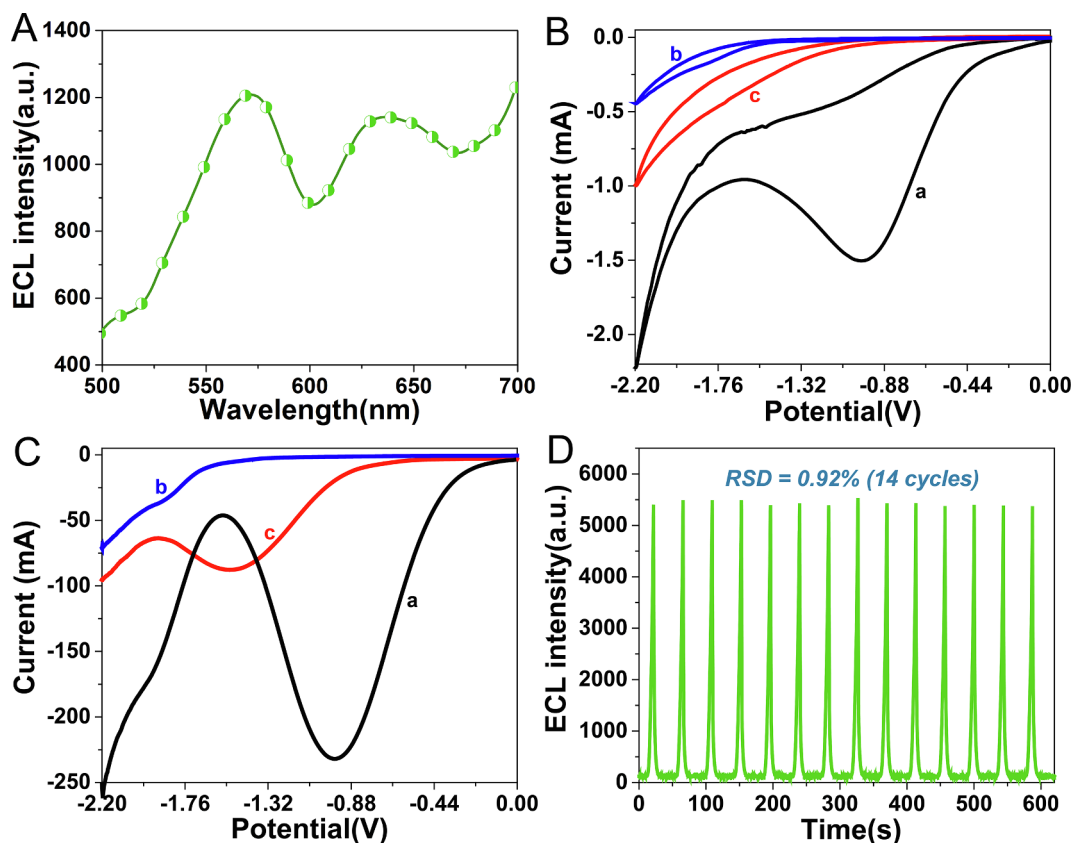
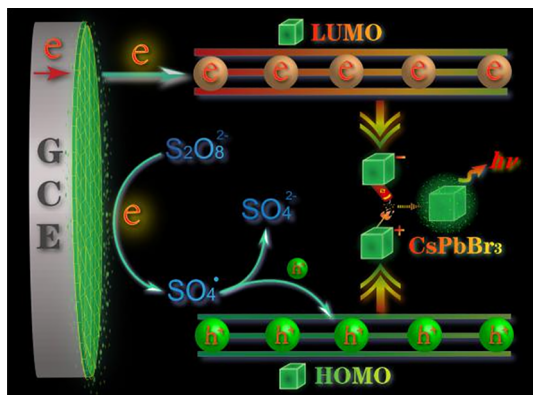


Fig. 3. (A) Cathodic ECL spectra of CsPbBr₃ NCs|GCE in 0.1 M pH 7.4 PBS containing 0.1 M K₂S₂O₈. (B) CVs of (a) bare GCE and (b,c) CsPbBr₃ NCs|GCE in 0.1 M pH 7.4 PBS (b) in absence of K₂S₂O₈ and (a,c) containing 0.1 M K₂S₂O₈ at 0.1 V/s. (C) DPVs of (a) bare GCE and (b,c) CsPbBr₃ NCs|GCE in 0.1 M pH 7.4 PBS (b) in absence of K₂S₂O₈ and (a,c) containing 0.1 M K₂S₂O₈. (D) ECL emission from CsPbBr₃ NCs|GCE in 0.1 M pH 7.4 PBS containing 0.1 M K₂S₂O₈ under continuous cyclic scans in the range 0 to -2.2 V at 0.1 V/s.



Scheme 1. The cathodic ECL mechanism of the CsPbBr₃ NCs in an aqueous medium.

The CsPbBr₃ NCs in hexane emitted green fluorescence under visible light while displaying a brighter greenish PL under UV light (inset of Fig. 1A). Transmission electron microscopy (TEM) shows regular and homogeneous cubic-shaped crystals with an average edge length of around 8 nm for the CsPbBr₃ (Fig. 1B). Furthermore, the peaks corresponding to Cs, Pb and Br elements in the EDX pattern confirmed the elementary composition of the NCs (Fig. 1C).

We investigated the cathodic ECL behavior of the CsPbBr₃ NCs using a GCE in an air-saturated aqueous medium with K₂S₂O₈ as coreactant. A strong ECL signal was obtained on the CsPbBr₃ NCs|GCE in the presence of K₂S₂O₈ (Fig. 2A, curve a), compared to that without K₂S₂O₈ (Fig. 2A, curve b). To gain a better understanding of the ECL generation, we also

investigated the ECL performance in the absence of CsPbBr₃ NCs. As expected, a weak ECL signal was observed at the bare GCE (Fig. 2A, curve c), which was consistent with previously reported studies [17]. In addition, the ECL spectrum of CsPbBr₃ NCs|GCE in the presence of K₂S₂O₈ displayed two obvious peaks at 570 nm and 640 nm (Fig. 3A). It was speculated that the sharp emission peak at 570 nm corresponded to CsPbBr₃ NCs, being broader and showing an obvious red shift compared to the PL spectrum [18]. The small emission peak at 640 nm suggested that the ECL of the CsPbBr₃ NCs/S₂O₈²⁻ system also contained emissions from an oxygen-containing species [19]. The presented CsPbBr₃ NCs/S₂O₈²⁻ ECL system has potential for biological applications due to low biological background luminescence and tissue absorption in the present region.

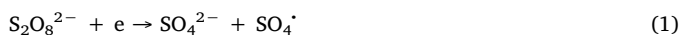
CH₃NH₃PbBr₃ NCs have been reported as excellent perovskite-based ECL luminophores in an organic medium [20]. However, it's worth noting that a weak ECL emission can be observed on CH₃NH₃PbBr₃ NCs|GCE in 0.1 M pH 7.4 PBS containing 0.1 M K₂S₂O₈ (Fig. 2B, curve a). Meanwhile, the ECL intensity of CsPbBr₃ NCs|GCE in 0.1 M pH 7.4 PBS containing 0.1 M K₂S₂O₈ (Fig. 2B, curve b) was twice as high as that of CH₃NH₃PbBr₃ NCs in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) and 5 mM benzoyl peroxide (BPO) (Fig. 2B, curve c). All the above results indicate that CsPbBr₃ NCs and S₂O₈²⁻ can form an excellent cathodic ECL system in aqueous medium. By contrast, organometallic halide perovskites prepared in the organic phase cannot achieve this outcome, indicating the potential advantages of the presented ECL system in terms of new applications.

The ECL quantum efficiency (Φ_{ECL}) is an important parameter in the evaluation of ECL probes. The Φ_{ECL} of CsPbBr₃ NCs was calculated to be 1.6% [21,22], which suggested that CsPbBr₃ NCs could be promising

candidates as ECL luminophores for ECL emitters and sensing.

The electrochemical responses were recorded simultaneously to explore the ECL mechanism. Compared with a bare GCE in the absence of $K_2S_2O_8$, the cathodic peak around -1.0 V on the bare GCE in 0.1 M pH 7.4 PBS containing 0.1 M $K_2S_2O_8$ (Fig. 3B, curve a) indicated the electrochemical reduction of $S_2O_8^{2-}$ to the strongly oxidizing intermediate sulfate radical anion ($SO_4^{\cdot-}$), followed by injection of holes into the HOMO of the NCs to produce $CsPbBr_3 NC^+$ for coreactant ECL (Fig. 3B, curve c) [18]. Although no obvious electrochemical reduction peak was observed by CV on the $CsPbBr_3 NCs|GCE$ in $S_2O_8^{2-}$ solution (Fig. 3B, curve c) due to the poor conductivity of the $CsPbBr_3 NCs$ and low sensitivity of the CV method, we can observe an obvious cathodic peak at approximately -1.5 V with an onset potential around -1.32 V (Fig. 3C, curve c) from the DPV response, which corresponds to the ECL performance. The results also indicated that $CsPbBr_3 NCs$ could be electrochemically reduced to a negatively charged state ($CsPbBr_3 NC^-$) by injecting electrons into the LUMO. The results demonstrate that hole and electron injection processes play a prominent role in generating the ECL intensity of $CsPbBr_3 NCs$ in the present ECL system.

We speculated that the ECL emission mechanism was caused by electron transfer annihilation between the electroreduction product $CsPbBr_3 NC^-$ and the oxidation product $CsPbBr_3 NC^+$ by $SO_4^{\cdot-}$. The excited state $CsPbBr_3^*$ was subsequently generated via electron transfer, leading to intense ECL emission via a radiative pathway by emitting a photon. The possible ECL mechanism is described by the following equations (Scheme 1) [20]:



The ECL intensity of the $CsPbBr_3 NCs|GCE$ remained constant under consecutive potential scans in 0.1 M pH 7.4 PBS containing 0.1 M $K_2S_2O_8$, with a relative standard deviation (RSD) of only 0.92% (Fig. 3D). We reason that the OA and OLA facilitated superlattice formation through cross-linking of the long carbon chains by hydrophobic interaction, which prevented the intrusion of polar solvents and improved the stability of the NC film in aqueous solution [13]. The above results demonstrate that the ECL emission of $CsPbBr_3 NCs|GCE$ is highly repeatable and stable.

4. Conclusions

In conclusion, a high-performance cathodic ECL emission based on $CsPbBr_3 NCs$ in aqueous solution was reported. We speculated that the ECL emission mechanism was the electron transfer annihilation pathway between the electro-redox product $CsPbBr_3 NC^-$ and $CsPbBr_3 NC^+$. The ECL spectrum and the stability of the $CsPbBr_3 NC$ -based ECL probe suggest potential applications of the studied system in ECL assays. This study also established a framework for design of other perovskite-based ECL probes.

CRediT authorship contribution statement

Huaping Peng: Project administration, Writing - review & editing, Supervision. **Weihua Wu:** Conceptualization, Data curation, Writing - original draft, Software, Validation. **Zhongnan Huang:** Data curation,

Writing - original draft. **Luyao Xu:** Methodology, Software. **Yilun Sheng:** Software, Validation. **Haohua Deng:** Data curation. **Xinghua Xia:** Writing - review & editing. **Wei Chen:** Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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