Electronic Supplementary Information

Size-selected and surface-passivated CsPbBr₃ perovskite nanocrystals for self-enhanced electrochemiluminescence in aqueous media

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Instruments

Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectrometry were obtained by an S-4800 scanning electron microscope (Hitachi Ltd., Japan). Transmission electron microscopy (TEM) images were obtained with a JEM-2100 transmission electron microscope (JEOL Ltd., Japan). X-ray photoelectron spectroscopy (XPS) was conducted with an ESCALAB250Xi spectrometer (Thermo Fisher Scientific Co., USA). The UV-visible absorption spectra were supplied by a UV-3600 U-vis spectrophotometer (Shimadzu, Japan). PL spectra were tested using an F-7000 spectrophotometer (Hitachi, Japan). Electrochemical impedance spectroscopy (EIS) was recorded by a Thales electrochemical workstation (Zahner-elektrik GmbH & Co. KG, Germany) with a three-electrode system in the buffer including 1 mM PBS, 0.1 M KCl and 5.0 mM K_3 [Fe(CN)₆/K₄[Fe(CN)₆]. The amplitude of the applied sine wave potential was 5 mV, and the frequency range was from 0.01 Hz to 100 kHz at a bias potential of about 200 mV. PL lifetime was recorded by a PL spectrometer FLS980 (Edinburgh, England). Zeta potential analysis was conducted with a 90Plus Dynamic Light Scattering Instrument (Brookhaven Instruments Corporation, USA). The static water contact angle images were captured with an OCA 30 contact angle meter (Dataphsics Instruments Gmbh. Germany) using droplets of the distilled water at 25 °C. Fourier transform infrared (FTIR) spectra were measured with a Nicolet 6700 spectrophotometer (Nicolet Co., USA). EC data and ECL signal were collected by a CHI 660D electrochemical analyzer (Shanghai CH Instruments Co., ltd., China) and a

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Model MPI-E Electrochemiluminescence Analyser (Xi'an Remex Analytical Instrument Co., Ltd., Xi'an, China), respectively.

Quantum yield measurement

The photoluminescence quantum yields (PLQYs) of LCPB hexane dispersions were measured by a standard method^{S1} with a reference dye (quinine sulphate in 0.1 M H_2SO_4 , PLQY=58 %), and PLQYs were calculated according to the following formula:

$$\Phi_{x} = \Phi_{r} \left[\frac{A_{r}}{A_{x}} \right] \left[\frac{n_{x}^{2}}{n_{r}^{2}} \right] \left[\frac{D_{x}}{D_{r}} \right]$$
(1)

" Φ , *A*, *n*, and *D*" represent the PLQY, absorbance of the solution, the refractive index of the solution, and the integrated PL intensity, and subscripts "*r*" and "*x*" represent samples and references, respectively. It has to make sure that both the quinine sulfate and the NCs were in sufficient dilutions to keep the optical absorbance below 0.05 in order to minimize self-absorption.

Synthesis of HCPB^{S2}

 Cs_2CO_3 (0.2035 g), ODE (10 mL), and OA (0.625 mL) were mixed into a 3-neck flask (25 mL), which was dried for 1 h at 100 °C in vacuum, and then heated to 150 °C for about 40 min under N₂ atmosphere until a transport solution was obtained (precursor solution). PbBr₂ (0.276 g) and ODE (20 mL) were loaded in a 3-neck flask (100 mL),

dried for 1 h at 100 °C in vacuum. After further adding pre-dried OAm (2 mL) and OA (2 mL), the mixture degassed at 120 °C for 30 min and further heated to 150 °C under nitrogen flow. 2.0 mL of precursor solution was quickly injected into the reaction solution, which was cooled with an ice-water bath after 5 s. The crude solution was centrifuged at 8000 rpm for 10 min and washed with EAC once. The final products were dispersed in hexane.

Electrochemistry behaviours of OAm and bare GCE



Fig. S1 Anodic DPV profiles of OAm (red) and blank (black) in EAC containing 0.1 M TBAPF₆.



Fig. S2 Cathodic DPV profiles of bare GCE in air, N₂, and O₂ -saturated PBS.

LCPB versus HCPB



Fig. S3 (A) ECL responses of HCPB|GCE in PBS or EAC containing 0.1 M TBAPF₆ with or without coreactant of TPrA (10 mM). (B) LSV waves of LCPB|GCE (black) and HCPB|GCE (red).



Fig. S4 (A) TEM image, (B) XRD pattern, and (C) optical characterizes of HCPB.

TEM image showed that HCPB were regular nanocubes with a size of about 8-9 nm. The XRD pattern of HCPB was consistent with the standard card (PDF#54-0752)

of CsPbBr₃ with cubic phase. The absorption and PL emission peaks of HCPB were centred at 490.9 nm and 511.2 nm, respectively.



Fig. S5 (A) Nyquist plots of EIS and (B) contact angle images of HCPB (a) and LCPB

(b) modified GCE and glass substrate, respectively.



Solvent regulation

Fig. S6 Size distributions of LCPBs through solvent regulation with hexane contents of 0, 1, 2, 3, 4, 5, 10, and 30% (a-h, respectively).



Fig. S7 (A) UV-vis absorption peak position and stokes shift data, and (B) PL emission peak position and FWHM data of the size-selected LCPBs through solvent regulation with hexane contents from 0 to 50 %.

Table S1. Detailed atoms percentage contents of the pristine LCPB and TOP-capped

 LCPB by XPS.

Elements	LCPB %	LCPB-TOP %
Cs	3.62	2.25
Pb	3.68	2.27
Br	11.32	6.75
С	71.89	78.59
Ν	1.99	1.30
0	7.5	7.26
Р	/	1.58



Fig. S8 XPS analyses of N 1s (a), Cs 3d (b), and Pb 4f (c) of pristine LCPB and TOPcapped LCPB corresponding to the lower and upper curves in each graph.

ECL spectra of LCPBs



Fig. S9 Fitting process of ECL spectrum of pristine LCPB.



Fig. S10 Fitting process of ECL spectrum of LCPB-TOP.

ECL efficiency calculation

ECL efficiency^{S3} was calculated by comparing the integrated ECL intensity (emitted photons) and the current value (consumed charges) of the self-enhanced LCPB samples with those of the standard $Ru(bpy)_3^{2+}$ -TPrA system under same experimental conditions using the following equation:

$$\Phi_{x} = 100 \left(\frac{\int_{a}^{b} ECL \, dt}{\int_{a}^{b} Current dt} \right) \sqrt{\frac{\int_{a}^{b} ECL \, dt}{\int_{a}^{b} Current \, dt}}, \quad (2)$$

Where Φ is the quantum yield (%) relative to a reference system, ECL is the ECL intensity, current is the electrochemical current value, r is the reference system $(\text{Ru}(\text{bpy})_3^{2+}\text{-TPrA})$, and x is the sample (LCPB).

The ECL-time curve and current-time curve were acquired with linear sweep voltammetry from 0 to +2.0 V. The ECL of reference was collected in PBS (0.1 M, pH=7.4) containing 1.0 μ M of Ru(bpy)₃²⁺ and 10 mM of TPrA. The ECL of samples were acquired with LCPB (8.0 μ L, 0.5 mg mL⁻¹) modified GCE in PBS (0.1 M, pH=7.4) without any extra coreactant.



Fig. S11 ECL-time and current-time curves of $Ru(bpy)_3^{2+}$ -TPrA system and selfenhanced LCPB in PBS.

	Integral areas		ECL efficiency
	ECL-time	Current-time	(%)
$Ru(bpy)_3^{2+}$ -TPrA (PBS=7.4)	46165.71	6.7295	/
Pristine LCPB (PBS=7.4)	2575.4	5.0262	7.47
Improved LCPB (PBS=7.4)	13478.38	3.4423	57.08

 Table S2. Detailed data for the calculation of ECL efficiencies.

Stability of the prepared LCPB



Fig. S12 Photographs for LCPB hexane solution at different processing stages including pristine (LCPB), EAC-washed (LCPB-EAC), and TOP-capped LCPB (LCPB-TOP) stored in a refrigerator at 4 °C for twenty days.



Fig. S13 PL stability curves for LCPBs at different processing stages under ambient conditions.



Fig. S14 Zeta potentials of LCPBs at different processing stages.

To shed more light on the reason for the enhanced storage stability, we quantified their zeta potentials (Fig. S14). The pristine NCs showed a negative value of about - 22.51 mV, confirming the adsorption of ligands on the NCs surface.^{S4} After the NCs were washed with EAC, the value reduced to about -12.94 mV, suggesting partial desorption of surface ligands, which resulted in the worst storage stability. Upon passivated with TOP, the NCs showed a positive value of about +36.62 mV. Such a

high zeta potential coupled with the large steric hindrance of TOP was responsible for the excellent stability of TOP-capped NCs dispersion.



Fig. S15 SEM images of pristine LCPB (a) and LCPB-TOP (b) constructed solid films.

Other LCPB-based ECL systems



Fig. S16 ECL-potential curves (0-1.0 V) of the improved LCPB|GCE in PBS with various additives including TPrA (1 mM), AA (1 mM), and H_2O_2 (5 mM), respectively.

Mechanism of LCPB-AA ECL system

We redefined AA as H_2AA to facilitate the subsequent description of possible ECL mechanism. H_2AA (pK_{a1} = 4.17) could easily lose one proton in PBS (Reaction 3).

Then HAA⁻ was oxidized to ascorbate radical (HAA⁺) in the positive scanning (Reaction 4), which deprotonated subsequently to form ascorbate anion radical (AA⁻⁺) because HAA⁺ was still a strong acid ($pK_{a3} = -0.45$) (Reaction 5).^{S5} Then, LCPB could be chemically reduced by AA⁻⁺ to produced one reduced state (Reaction 6). Meanwhile, LCPB were electrochemically oxidized to oxidized states (Reactions 7-9), and the rapid charge transfer between the reduced and oxidized LCPBs generated excited state of [LCPB]* (Reactions 10-12), which finally emitted ECL during its relaxation process (Reaction 13).

$$H_2AA - H^+ \longrightarrow HAA^- (pK_{a1} = 4.17, pK_{a2} = 11.57)$$
 (3)

$$\mathrm{HAA}^{-} - \mathrm{e} \longrightarrow \mathrm{HAA}^{*} \tag{4}$$

$$HAA^{\bullet} - H^{+} \longrightarrow AA^{\bullet} (pK_{a3} = -0.45)$$
(5)

$$[LCPB] + AA^{-} \rightarrow [LCPB]^{-} + AA \tag{6}$$

$$[LCPB] - e \longrightarrow [LCPB]^{+}$$
⁽⁷⁾

$$[LCPB]^{+\bullet} - e \longrightarrow [LCPB]^{2+\bullet}$$
(8)

$$[LCPB]^{2+\bullet} - e \longrightarrow [LCPB]^{3+\bullet}$$
(9)

$$[LCPB]^{\bullet\bullet} + [LCPB]^{3+\bullet} \longrightarrow [LCPB]^{*} + [LCPB]^{2+\bullet}$$
(10)

$$[LCPB]^{-\bullet} + [LCPB]^{2+\bullet} \longrightarrow [LCPB]^{*} + [LCPB]^{+\bullet}$$
(11)

$$[LCPB]^{\bullet\bullet} + [LCPB]^{+\bullet} \longrightarrow [LCPB]^{\bullet\bullet} + [LCPB]^{0}$$
(12)

$$[LCPB]^* \rightarrow [LCPB] + hv \tag{13}$$

Optimization experiments



Fig. S17 (A) ECL responses of the LCPB|GCE modified with different volumes of LCPB dispersion; (B) ECL responses of the LCPB|GCE acquired with different potential scanning ranges. (C) ECL responses of the LCPB|GCE measured in different buffer solutions with various pH values.

The optimization experiments were conducted to achieve the best ECL performance. The amount of LCPB dispersion utilized to modify the GCE surface is a major factor deciding whether a solid ECL film can be self-assembled successfully. Insufficient amount may lead to an incomplete solid film which could be easily destructed by water, while too much sample may hinder electron transport. As shown in Fig. S17A, LCPB dispersion with dosages from 5.0 to 9.0 μ L were dropped on the surface of GCEs, and 8.0 μ L was the best volume to construct an excellent LCPB solid film.

The applied potential also plays a decisive role in ECL measurements. We optimized the scanning potential in the range of 0-1.0 V, 0-1.2 V, 0-1.4 V, and 0-1.6 V, respectively. As depicted in Fig. S17B, only 0-1.0 V potential range can maintain the persistent ECL stability. The increased potential range caused a rapid drop in the ECL signal. Therefore, 0-1.0 V was chosen as the best applied voltage.

The system pH is another crucial factor affecting ECL performance. The experiment results showed that the ECL signals could be produced in both acidic and alkaline conditions, and the strongest ECL signal appeared under weak alkalinity (Fig. S17C), which was mild to NCs and beneficial for the deprotonating of coreactant. Thus, pH=7.4 was utilized as the best condition.



Actual ECL response curves

Fig. S18 Actual ECL responses of the improved LCPB|GCE to different concentrations of (A) H₂O₂, (B) AA, and (C) HeLa cells, respectively.

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