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J. Am. Chem. Soc., Just Accepted Manuscript • Publication Date (Web): 09 Jun 2017

Downloaded from http://pubs.acs.org on June 10, 2017

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# Electrochemistry and Electrochemiluminescence of Organometal Halide Perovskites Nanocrystals in Aqueous Medium

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ABSTRACT: The redox nature and electrochemiluminescence (ECL) of highly crystalized organometal halide perovskites CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> nanocrystals (NCs) in aqueous medium were investigated for the first time. CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs could be electrochemically reduced to negative charged states by injecting electrons onto the lowest unoccupied molecular orbitals and oxidized to positive charged states by removing electrons from the highest occupied molecular orbitals, the charge transfer between NCs of positive charged states and negative charged states could bring out ECL. Redox sequence of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs played an important role on the generation of charge transfer involved ECL, transient ECL could only be achieved by electrochemically reducing the positive charged NCs in annihilation route. Large redox current was unfavorable for the ECL, charge mobility within CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs displayed important effect on ECL intensity in coreactant route, which was promising for photovoltaic and optoelectronic devices. Importantly, ECL spectra of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs were almost identical to the photoluminescence spectrum with maximum emission around 535 nm and FWHM around 25 nm, which might open a way to monochromatic ECL with highly crystalized NCs as emitters and was promising for the color-selective ECL analysis.

### INTRODUCTION

Hybrid organometal halide perovskites, with the common formation AMX<sub>3</sub> (A is an organic cation, M is a metal cation, and X is a halogen anion), are of great interest in photovoltaic and optoelectronic devices.<sup>1-6</sup> A certified power conversion efficiency as high as 22.1% has been achieved with the organometal halide perovskite based solar cells.<sup>5</sup> Along with investigation on the charge mobility,<sup>7,8</sup> carriers lifetime,<sup>9</sup> carrier diffusion length,<sup>10</sup> and carriers recombination dynamics<sup>1</sup> within organometal halide perovskites, the high absorption coefficient,<sup>12</sup> high photoluminescence (PL) quantum yield,<sup>13,14</sup> narrow full width at half maximum (FWHM), and wide wavelength tunability<sup>13,15</sup> features also made hybrid halide perovskites promising for optoelectronic devices.<sup>2,4</sup> Unfortunately, the poor long-term stability against ultraviolet irradiation and water blocked their possible applications under normal condition.<sup>5</sup> The intrinsic affinity of AMX<sub>3</sub> for moisture might lead to degradation process,<sup>16,17</sup> many open questions about their redox and charge transfer natures in aqueous medium still remain.

Electrochemiluminescence (ECL) was the light emitting process whose exited states were generated by the energetic electron transfer occurred in the vicinity of working electrode.<sup>18</sup> Ding and Bard first investigated the redox nature of Si NCs with ECL technology.<sup>19</sup> They found that Si NCs could be electrochemical reduced by injecting electrons onto the lowest unoccupied molecular orbitals (LUMO) and oxidized by removing electrons from the highest occupied molecular orbitals (HOMO), Si NCs could store both positive and negative charges under electrochemical condition, and subsequently lead to ECL upon charge transfer.<sup>19</sup> Although ECL has been extensively utilized to investigate the redox nature of various <sup>20-26</sup> only very recently, Huang demonstrated that perov-NCs,<sup>2</sup> skites CsPbBr<sub>3</sub> NCs could be electrochemically oxidized (or reduced) to different charged states and bring out highly monochromatic ECL in organic medium upon the charge transfer between NCs of positive charged states and negative charged Instrument Co., Ltd. China) using a three-electrode system ACS Paragon Plus Environment

states.<sup>27</sup> Herein, the electrochemical redox and charge transfer natures of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs in aqueous medium were investigated by ECL from CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs modified glass carbon electrode (GCE), i.e. CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE.

#### **EXPERIMENTAL SECTION**

Chemicals and Materials. All chemicals were of analytical grade. All aqueous solutions were prepared with doubly distilled water (DDW). Methylamine (CH<sub>3</sub>NH<sub>2</sub>, 30%-33% in methyl alcohol), hydrobromic acid (HBr, 40%), lead bromide (PbBr<sub>2</sub>, 99%), n-octylamine (C<sub>8</sub>H<sub>19</sub>N, 99%,), oleic acid (OA, AR), tri-n-propylamine (TPrA, >99%) were purchased from Aladdin. N-N-dimethylformamide (DMF, AR), potassium phosphate monobasic (KH<sub>2</sub>PO<sub>4</sub>, AR), di-potassium hydrogen phosphate trihydrate (K<sub>2</sub>HPO<sub>4</sub>•3H<sub>2</sub>O, AR), potassium chloride (KCl, AR), ammonium persulfate  $((NH_4)_2S_2O_8, AR)$  were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ether absolute (AR) was obtained from Fuyu Fine Chemical Co., Ltd. (Tianjin, China). Hydrochloric acid (HCl, AR) was obtained from Laiyang Economic and Technological Development Zone Fine Chemical Plant (Shanghai, China). Toluene (AR) was purchased from Laiyang Kant Chemical Reagent Co., Ltd. (Shandong, China).

Apparatus and Characterizations. Scanning electron microscopy (SEM) was obtained with a SUPRA 55 field emission scanning electron microscope (Carl Zeiss AG, Germany). Ultraviolet-visible (UV-vis) absorption spectrum was recorded on a TU-1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China). PL analysis was measured with F-320 spectrofluorimeter (Tianjin Gangdong Sci&Tech Development Co., Ltd., China), X-ray diffraction (XRD) pattern was recorded using an X-ray diffractometer (Bruker AXS D8 Advance, Germany) with Cu Ka radiation ( $\lambda$ =1.5418Å). Differential pulse voltammetry (DPV) was recorded with a CHI 822 electrochemical analyzer (Shanghai, China). The ECL was conducted on a MPI-A ECL analyzer (Xi'an Remex Analytical

including a GCE working electrode, a Pt-wire counter electrode, and an Ag/AgCl (saturated) reference electrode. The photomultiplier tube was biased at 800 V. ECL spectra were recorded with a homemade ECL spectrum system,<sup>28,29</sup> which could synchronously trigger and operate VersaSTAT 3 analyzer and CCD-coupled monochromator.

**Preparation of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs and CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE.** CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs were synthesized according to literature.<sup>30</sup> Briefly, 15 mL of methylamine was cooled to 0 °C with continuous stirring, and 14.25 mL HBr was added slowly. After stirring for 1 h, the mixture was rotary evaporated at 50 °C, the precipitate were washed and centrifuged with diethyl ether for three times, CH<sub>3</sub>NH<sub>3</sub>Br was obtained by drying the precipitate under vacuum. 0.64 mmol CH<sub>3</sub>NH<sub>3</sub>Br and PbBr<sub>2</sub>, 500 µL oleic acid and 25 µL n-octylamine were dissolved into 5 mL DMF, and then slowly transferred into 30 mL toluene under stirring. 2 h later, the final solution was centrifugation at 6000 rpm for 5 min, the obtained yellow precipitates, i.e. CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs, were stored under darkness condition.

The  $CH_3NH_3PbBr_3$  NCs were ultrasonically dispersed into toluene (0.030 g/mL). Then 10  $\mu$ L of the suspension was cast onto GCE to form  $CH_3NH_3PbBr_3$  NCs|GCE.



**Figure 1.** (A) UV–vis absorption and PL ( $\lambda$ ex: 380 nm) spectra of monodispersed CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs in toluene; (B) SEM pattern of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE; Inset: SEM pattern of bare GCE.

## **RESULTS AND DISCUSSION**

#### Characterization of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>NCs and CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE

The perovskites CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs displayed an obvious excitonic peak at 526 nm (2.35 eV) on absorption spectrum and a sharp PL peak around 531 nm (2.34 eV) with FWHM of 22 nm on PL spectrum (Figure 1A). The small Stokes shift implied that the PL was originated from direct-gap recombination.<sup>1</sup> XRD pattern (Figure S1A) of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs displayed several peaks at 20 values of 14.9°, 21.3°, 30.1°, 33.9°, 37.2°, 43.1°, 46.0°, and 48.5°, respectively, which was almost the same to those of bulk CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> materials.<sup>3,10,30,31</sup> The well-defined XRD pattern not only indicated the perfect structure cell of as-prepared CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs without obvious defects, but also confirmed that CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs were of cubic crystal structure with the cation lead in the center of an octahedron formed by six bromide ions, while the methyl ammonium cations were embedded in the voids of a set of corner-sharing PbBr<sub>6</sub> octahedra (Inset of Figure S1).<sup>3,32,33</sup> The broadness of the peaks on XRD pattern manifested that CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs was smaller than bulk CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>. The morphology pattern of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE (Figure 1B and Figure S1B) not only demonstrated that CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs were nanowires of 500 $\pm$ 300 nm  $\times$  50 $\pm$ 20 nm size and uniformly distributed on GCE surface, but also further proved the CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs were highly crystalized with

well-defined perovskites structure. The absorption and PL spectra were almost identical to the CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs of the same size in literature.<sup>31</sup>



Figure 2. (A) anodic DPV of (a) GCE and (b)  $CH_3NH_3PbBr_3$  NCs|GCE in air-free 0.10 M pH 7.4 PBS; (B) anodic CV and (C) ECL of (a) GCE and (b, c)  $CH_3NH_3PbBr_3$  NCs|GCE in air-free 0.10 M pH 7.4 PBS containing (a, b) 10.0 and (c) 0.0 mM TPrA at 100 mV/s. Inset: anodic ECL spectra of (a) GCE and (b)  $CH_3NH_3PbBr_3$  NCs|GCE in air-free 0.10 M pH 7.4 PBS containing 10 mM TPrA.

#### Electrochemistry and Coreactant ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE

Several groups demonstrated that the deliberately injected charges in polycrystalline perovskite films could exhibit remarkably long lifetime, long diffusion length, and high in-tra-grain carrier diffusivity.<sup>8-10,34</sup> When comparted with bare GCE, DPV of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE in phosphate buffer solution (PBS) displayed a weak anodic process with onset potential around +0.69 V and maximum response around +0.87 V (Figure 2A), which indicated that CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>NCs could be electrochemically oxidized to positive charged states ( $R^+$ , cation radical) in PBS by removing electrons from HOMO.<sup>19</sup> Both DPV (Figure 2A, curve b) and cyclic voltammetry (CV) response (Figure 2B, curve c) of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>NCs|GCE were very weak in blank PBS, the efficiency for removing electrons from HOMO of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs might be low. TPrA was employed to investigate the anodic redox nature of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>, because TPrA could be oxidized to TPrA<sup>++</sup>, then underwent deprotonation to produce TPrA' ( $E^{\circ} = -1.7 \text{ eV}$ ),<sup>18,35</sup> which could inject electrons onto LUMO of NCs to produce negative charged NCs (R, anion radical) for coreactant ECL.<sup>20</sup> TPrA displayed strong oxidation current on bare GCE with onset around +0.60 V and no ECL was detected (Figure 2B&2C, curve a). The oxidation of TPrA was almost completely blocked between 0.60 and 1.20 V on CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE (Figure 2B, curve b), the CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> nanocrystal film of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE apparently blocked the direct charge transfer for oxidizing TPrA on GCE. Interestingly, CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE also displayed strong anodic ECL with onset potential around +0.69 V and the maximum emission around +1.20 V in the presence of TPrA (Figure 2C, curve b). The onset potential for ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE in PBS containing TPrA (Figure 2C, curve b) was almost the same to that for oxidizing CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE in blank PBS (Figure 2A, curve b), thus mobility of positive charge

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within CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> nanocrystal film might play an important role on oxidizing TPrA to TPrA'. Eqs1-5 embodied the coreactant ECL at anode:

$$R - e \rightarrow R^{+}$$
(1)  
TPrA - e  $\rightarrow$  [TPrA']<sup>+</sup>  $\rightarrow$  TPrA' + H<sup>+</sup> (2)

(3)  $R + TPrA' \rightarrow R'$ 

 $R^+ + R^- \rightarrow R^*$ 

$$R^{+} + R^{-} \rightarrow R^{*}$$
(4)  

$$R^{*} \rightarrow R + hv$$
(5)

The increasing current with potential beyond 1.20 V might due to the accumulation of positive charges within the CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> nanocrystal film of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE with positive scanned potential. As high-current-density was unfavorable for the radiative charge transfer<sup>36</sup> and electric-field-induced light emission,<sup>37</sup> lowered ECL was obtained with potential beyond +1.2 V (Figure 2C, curve b). The anodic ECL spectrum of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE displayed a sole and symmetric peak around 535 nm with FWHM of 25 nm (Inset of Figure 2C). The FWHM was smaller than those of traditional ECL emitters, <sup>18</sup> such as luminol and  $Ru(bpy)_3^{2+}$ , and even some highly passivated NCs with promising monochromatic ECL emission, such as dual-stabilizers-capped CdTe and CdSe NCs.  $^{29,38,39}$ 



Figure 3. (A) cathodic DPV of (a) GCE and (b) CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE in air-free 0.10 M pH 7.4 PBS; (B) cathodic CV and (C) ECL of (a) GCE and (b, c) CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE in air-free 0.10 M pH 7.4 PBS containing (a, b) 0.10 and (c) 0.0 M  $(NH_4)_2S_2O_8$  at 100 mV/s. Inset: cathodic ECL spectra of (a) GCE and (b) CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE in air-free 0.10 M pH 7.4 PBS containing 0.10 M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

When compared with bare GCE, DPV of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE in blank PBS also displayed a cathodic process with onset potential around -0.80 V (Figure 3A), indicating that CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs could be electrochemically reduced to negative charged states (R) by injecting electrons onto LUMO.  ${}^{19,27}$  S ${}_{2}O_{8}{}^{2}$  was employed to investigate the cathodic redox of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>, because S<sub>2</sub>O<sub>8</sub><sup>2-</sup> could be electrochemically reduced to a strong oxidizing intermediate, i.e.  $SO_4$  (E'  $\geq$ 3.15 V vs SCE), and then inject holes onto HOMO of NCs to produce  $R^+$  for coreactant ECL.  $^{19,20}$   $S_2O_8{}^{2-}$  displayed strong reduction current on bare GCE with onset around -0.30 V and maximum response around -1.0 V (Figure 3B, curve a). Although the reduction of  $S_2O_8^{2-}$  on CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE was obviously delayed with the onset negatively moved to  $\sim$  -0.60 V and maximum response negatively moved to  $\sim -1.30$  V (Figure

3B, curve b), respectively, the generation of  $R^+$  by oxidizing CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs with SO<sub>4</sub> apparently occurred ahead of generation of R<sup>-</sup> by electrochemically reducing CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs at cathode. The reductive current of  $S_2O_8^{2}$  on CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE was much stronger than the oxidative current of TPrA on CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE, probably due that mobility of electron was much higher than that of positive charge within perovskite NCs.<sup>40,41</sup> Because CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE displayed strong cathodic current for reducing  $S_2 O_8^2$ (Figure 3B, curve b), only weak ECL was observed upon the charge transfer between  $\mathbf{R}$  and  $\mathbf{R}^+$  at cathode.

$S_2O_8^{-2}$	$+ e \rightarrow SO_4^2 + SO_4^2$	(6)
_	<b>a</b>	

 $SO_4^{-} + R \rightarrow SO_4^{-} + R^+$ (7)

$$R + e \to R^- \tag{8}$$

$$\mathbf{R}^{-} + \mathbf{R}^{+} \to \mathbf{R}^{+} \tag{9}$$

The charge mobility within CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs demonstrated unneglectable effects on ECL intensity, both the anodic and cathodic coreactant ECL manifested that high redox current would lower the charge transfer involved ECL between R<sup>+</sup> and R. Cathodic ECL spectrum of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE (inset of Figure 3C) displayed a sharp and symmetric peak around 535 nm. Both anodic and cathodic coreactant ECL spectra were almost identical to PL spectrum of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs (Figure S2), indicating CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs were highly passivated without obvious defect surface states. As SEM and XRD have proved that CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs possessed perfect crystalized structure without obvious defects (Figure 1 & S1), these results might open a way towards highly monochromatic ECL with highly crystalized NCs as emitters.



Figure 4. Oxidative process started ECL transients of GCE (black line) and CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE (red line) in air-free 0.10 M pH 7.4 PBS by repetitively stepping potential from +1.50 V to (A) -1.30 V, (B) -1.0 V, (C) -0.80 V, and (D) -0.70 V, respectively, for 30 s at a frequency of 1 s. The blue lines indicate the stepping potentials. Inset: corresponding ECL spectra of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE by repetitively stepping the potential for 30 s (the data was accumulated results for three parallel measurements).

#### Annihilation ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE

The electrochemical energy required for oxidizing or reducing CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs were further verified by ECL transient technology,<sup>27</sup> because annihilation ECL could be generated upon the exergonic electron transfer between electrochemically reduced NCs and electrochemically oxidized NCs.<sup>15</sup> Figure 4 displayed the oxidative process started ECL transient

of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE. No ECL was observed by stepping CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE at +1.5 V for 1s in the initial step, because only holes was injected onto HOMO and only NCs of oxidative states were obtained. Obvious ECL was observed stepping CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE from +1.50 V to -1.30, -1.0, and -0.80 V, by respectively, indicating radiative charge transfer occurred by reducing CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs of oxidative states. No ECL was obtained by stepping potential from +1.50 V to -0.70 V (Figure 4D), the onset potential to electrochemical reduce CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE was deduced to be around -0.80 V, which was consisted with that obtained with DPV (Figure 3A). The onset potential for coreactant cathodic ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE was around -1.0 V (Figure 3C), which probably because large redox current was unfavorable for the radiative charge transfer.<sup>37</sup> Transient ECL spectra were almost the same to PL spectrum of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs, indicating excited states generated under different electrochemical bandgaps were the same to those for PL.

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**Figure 5.** Reductive process started ECL transients of GCE (black line) and  $CH_3NH_3PbBr_3 NCs|GCE$  (red line) in air-free 0.10 M pH 7.4 PBS by repetitively stepping potential from -1.60 V to (A) 1.20 V, (B) 1.0 V, (C) 0.70 V, and (D) 0.60 V respectively at a frequency of 1 s. The blue lines indicate stepping potentials. Inset: corresponding spectra for the annihilation ECL from  $CH_3NH_3PbBr_3 NCs|GCE$  by repetitively stepping the potential for 30 s (the data was accumulated results for three parallel measurements).

Figure 5 demonstrated the reductive process started transient ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE. No ECL was observed by stepping CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE at -1.6 V for 1s in the initial step, because only electron was injected onto LUMO of the NCs. However, no ECL was detected in all the potential stepping cycle by stepping CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE from -1.60 V to +1.20, +1.0, +0.80 V (Figure S3A) and +0.70 V, respectively, indicating radiative charge transfer could not occur by electrochemically oxidizing the negative charged CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs. The obvious ECL was observed in the followed steps by stepping CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE from +1.20, +1.0, +0.80 and +0.70 V to -1.60 V, respectively, which eventually proved that transient ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs could only be achieved by electrochemicaly reducing the positive charged NCs. Actually, both anodic and cathodic coreactant ECL also indicated that the oxidation of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs in advance was important for the charge transfer involved ECL in coreactant route (Figure 2 & 3). Thus, the redox se-

quence of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs played a crucial role on the generation of radiative charge transfer between CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs of positive charged states and negative charged states. Transient ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE was only achieved with oxidative process started redox processes, which was different from that of CsPbBr<sub>3</sub> NCs|GCE.<sup>27</sup> Importantly, life-time for the transient ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE was less than 80 ms (inset A, Figure S3A), which was also much shorter than that of CsPbBr<sub>3</sub> NCs|GCE (Figure S3B).<sup>27</sup> The Cs<sup>+</sup> or CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> located between the octahedras of cubic structure cell for perovskites NCs might have important effects on the radiative charge transfer of perovskites NCs. No ECL was obtained by stepping CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE from +0.60 V to -1.60 V (Figure 5D), the lowest electrochemical energy for oxidizing CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs was deduced to be around +0.70 V, which was similar to that obtained with DPV (Figure 2A). Spectra of the reductive process started transient ECL demonstrated a single peak with maximum intensity around 535 nm. which were almost the same to aforementioned ECL spectra of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs. Fortunately, transient ECL with greatly enhanced intensity and lifetime was obtained by stepping CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs|GCE from 0 V to +1.50 V in 0.1 M pH 7.4 PBS containing 10 mM TPrA (Figure S4). The flexible and adjustable ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs under varied electrochemical conditions was promising for photovoltaic and optoelectronic devices.

#### CONCLUSIONS

The electrochemical redox and ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs in aqueous medium were investigated for the first time. CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs could be electrochemically oxidized to positive charged states and reduced to negative charged states, respectively. Both coreactant and annihilation ECL proved that electrochemical redox reaction sequence played a crucial role on the ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs, i.e., the radiative charge transfer between CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs of positive charged states and negative charged states, because ECL from CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs were usually achieved by reducing CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs of positive charged states. CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs display flexible and adjustable ECL under varied electrochemical conditions, while spectral of all the ECL generated under different conditions were almost the same to PL spectrum with unmoved maximum emission wavelength and similar FWHM. CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs was promising for photovoltaic and optoelectronic device with impressive charge transfer and annihilation performance. The highly monochromatic ECL of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> NCs might also open a way to design novel ECL emitter with highly crystalized NCs for multiple-colored ECL assay.

## ASSOCIATED CONTENT

**Supporting Information**. XRD and SEM patterns, normalized ECL and PL spectra, ECL transients in control, and ECL transients with the presence of coreactant. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ACKNOWLEDGMENT

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This project was supported by the National Natural Science Foundation of China (Grant Nos. 21427808 and 21375077), the Fundamental Research Funds of Shandong University (Grant No. 2015JC037), and the Shandong Provincial Natural Science Foundation (ZR2014BM007).

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