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Citation: *Applied Physics Letters* **109**, 151101 (2016); doi: 10.1063/1.4964413

View online: <http://dx.doi.org/10.1063/1.4964413>

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Room-temperature electroluminescence from two-dimensional lead halide perovskites

Renzhi Li,¹ Chang Yi,¹ Rui Ge,¹ Wei Zou,¹ Lu Cheng,¹ Nana Wang,¹ Jianpu Wang,^{1,a)} and Wei Huang^{1,2}

¹Key Laboratory of Flexible Electronics (KLOFE) and Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China

²Key Laboratory for Organic Electronics and Information Displays and Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts and Telecommunications, 9 Wenyuan Road, Nanjing 210023, China

(Received 6 August 2016; accepted 24 September 2016; published online 10 October 2016)

Room-temperature electroluminescence (EL) is demonstrated from a light-emitting diode (LED) based on two-dimensional lead halide perovskites, $(\text{C}_6\text{H}_5\text{NH}_3)_2\text{PbI}_4$. The device has a multilayer structure of ITO/Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate)/ $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ /Bathophenanthroline/Al. The EL emission peaks at 526 nm with a narrow full width at half maximum of 15 nm, which originates from perovskite exciton emission. The LED device exhibits a maximum luminance of $\sim 9 \text{ cd m}^{-2}$ at a bias of 5 V. *Published by AIP Publishing.*

[<http://dx.doi.org/10.1063/1.4964413>]

Organic-inorganic halide perovskites have demonstrated great potentials in low-cost, high-performance optoelectronic devices owing to their superior light harvesting,¹ tailorable optical bandgaps,^{2,3} and excellent ambipolar charge transport properties.^{4,5} Three-dimensional (3D) lead halide perovskites have achieved a best certified power conversion efficiency (PCE) of $\sim 22\%$ in solar cells⁶ and an electroluminescence (EL) external quantum efficiency (EQE) as high as over 8% in light-emitting diodes (LEDs).⁷ However, the commercialization of perovskite optoelectronic devices still has a long way to go due to the issues of the 3D perovskite films, e.g., poor uniformity and stability.

Two-dimensional (2D) layered halide perovskites $(\text{RNH}_3)_2\text{PbX}_4$ have a sandwich-like structure formed by inserting the organic dielectric layers of RNH_3 into the neighbouring inorganic semiconductor layers of lead tetrahalide PbX_4 .⁸ The 2D perovskites naturally form a quantum-well structure with the inorganic semiconductor sheets of PbX_4 as wells and the organic layers as barriers. The 2D structure combined with the dielectric confinement effect enables the formation of stable excitons with large binding energy in inorganic semiconductor sheets, giving narrow and intense excitonic absorption and emission features with small Stokes shift.^{9,10} Moreover, compared to 3D analogues, the 2D perovskites are easier to form smooth, good surface coverage films by using spin-coating process,^{8,11} and exhibit improved thermal stability and moisture resistivity.^{8,11} Those properties makes the 2D perovskites favorable for optoelectronic device applications.

In 1990s, electroluminescence based on 2D perovskites were attempted, but it can only be observed at low temperatures and high voltages.^{12–14} Chondroudis and Mitzi¹⁵ fabricated room temperature EL devices by incorporating a quaterthiophene dye within lead halide perovskite layers,

which emit bright green-yellow light at room temperature originating from the quaterthiophene dye. Here, we use phenylmethanamine lead iodide ($(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$) (Fig. 1(a)) as an emitting layer to fabricate 2D perovskite light-emitting diodes (PeLEDs) with green emission. The visible 2D PeLEDs were turned on at room temperature, demonstrating a maximum luminance of $\sim 9 \text{ cd m}^{-2}$ at a bias of 5 V.

For optical characterizations, $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite films ($\sim 40 \text{ nm}$) are deposited on quartz glass substrates from the 10 wt. % precursor solution ($\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{I}$ and PbI_2 with 2:1 molar ratio in *N,N*-dimethylformamide (DMF)) at 6000 rpm for 30 s, followed by annealing at 130°C for 10 min. Fig. 1(b) presents the X-ray diffraction profiles of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite film. Well-defined diffraction peaks corresponding to the $(0\ 0\ 2l)$ (where $l = 1–6$) reflections, being at 5.66° , 11.08° , 16.52° , 22.00° , 27.54° , and 33.14° , can be clearly observed, suggesting the formation of the layered perovskite structure and a highly preferred orientation of inorganic sheets parallel to the substrate.^{8,16} After the perovskite film was exposed for 5 days at room temperature to ambient air of $\sim 50\%$ relative humidity, almost no change of X-ray pattern could be noticed, indicating a good moisture resistivity.

The optical absorption and emission spectra of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite thin film are presented in Fig. 1(c). The absorption spectrum shows two main features of a broad absorption at $\sim 382 \text{ nm}$ (3.24 eV) and a strong narrow peak at $\sim 516 \text{ nm}$ (2.40 eV). The former can be attributed to both higher order exciton transition energy levels and charge transfer transition between the organic and inorganic layers, and the latter narrow peak results from the intrinsic exciton absorption of the formed quantum well structure.^{17–19} The PL emission band is centered at 524 nm with a full-width at half-maximum (FWHM) of 16 nm, illuminating a Stokes shift of 37 meV. The small Stokes shift and narrow bandwidth suggest that the emission results

^{a)} Author to whom correspondence should be addressed. Electronic mail: iamjpwang@njtech.edu.cn

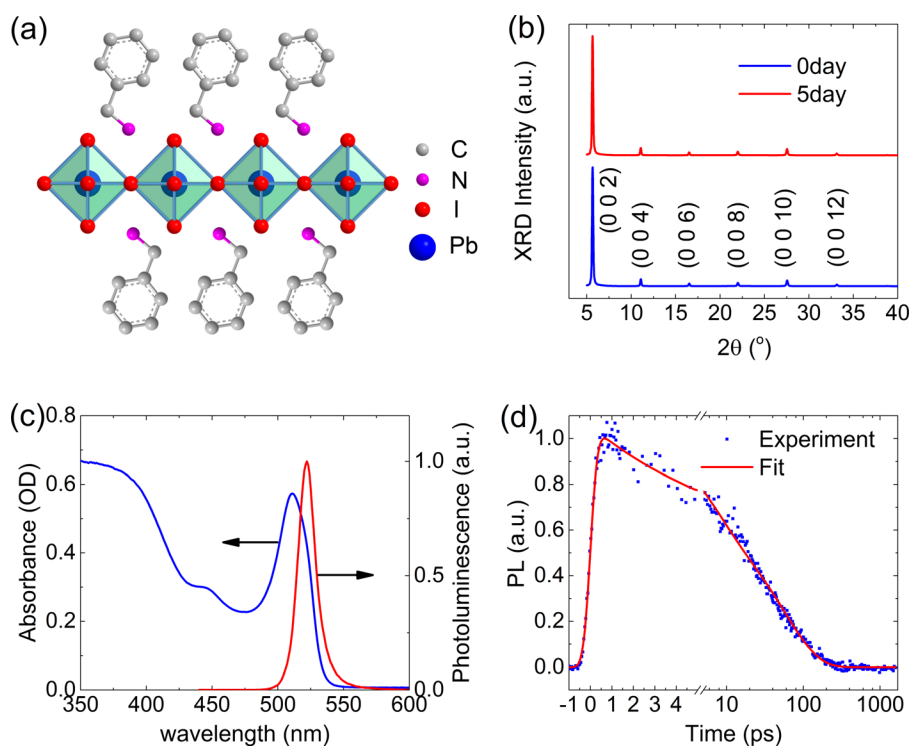


FIG. 1. (a) Chemical structure of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ layered perovskite. (b) X-ray diffraction profiles of a $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ film on a glass substrate. Blue and red lines show the data before and after exposure to atmosphere environment of $\sim 50\%$ relative humidity for 5 days, respectively. (c) Absorption and photoluminescence spectra of a $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite film spin-coated on a glass substrate. (d) Femtosecond PL decay trace of a $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite film spin-coated on a glass substrate. The pulse fluence of pump light at 410 nm was $10 \mu\text{J cm}^{-2}$. The probe wavelength was at 520 nm. The red line is fitting of normalized PL intensity (I_{PL}) via the two-exponential decay equation of $I_{\text{PL}} = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ where A_i and τ_i denote the fractional amplitudes and lifetimes, and $\sum_{i=1}^n A_i = 1$.

from recombination of the intrinsic exciton in the quantum well structure.

Fig. 1(d) shows the PL decay trace of a pristine perovskite film coated on a glass substrate. By using a double exponential decay function, we retrieved two lifetime values of 6.15 ps and 58.57 ps with fractional amplitudes of 0.39 and 0.61, respectively, obtaining an amplitude-averaged lifetime of 37.92 ps. The short PL lifetime can be attributed to the strong exciton-phonon interactions in the 2D perovskites at room temperature.^{20–23} Supplementary material Fig. S1 shows excitation-intensity-dependent PL quantum efficiency (PLQE) at room temperature. The PLQE is $\sim 0.5\%$ and exhibits almost no change in the large range of excitation intensity. We also measured the temperature-dependent photoluminescence (supplementary material Fig. S2) of a pristine perovskite film and found that the PL intensity became significantly higher at low temperatures. The above measurement results are consistent with the PL limited by the exciton-phonon quenching effect in the 2D perovskites.

We fabricated PeLEDs (Fig. 2(a)) with the multi-layered structure of ITO/Poly(3,4-ethylenedioxythiophene): Poly(styrenesulfonate) (PEDOT:PSS, 40 nm)/ $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ (40 nm)/Bathophenanthroline (Bphen, 7 nm)/Al (100 nm), where ITO/PEDOT:PSS and Al are anode and cathode, respectively, and Bphen is an electron transporting and hole blocking layer.²⁴ A ITO/glass substrate with a sheet resistance of $15 \Omega \text{sq}^{-1}$ was washed by deionized water, acetone, and isopropanol sequentially, followed by oxygen plasma treatment for 15 min.²⁵ A PEDOT:PSS thin film of 40 nm was spin-coated on the ITO glass substrate at 4000 rpm for 1 min and annealed in air at 150°C for 10 min, followed by depositing ~ 40 nm $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite film. The atomic force microscopy (AFM) measurement shows that the root-mean-square roughness (Rq) of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$

film on top of the PEDOT:PSS/ITO substrate is ~ 3.22 nm (Fig. 2(b)). The smooth and uniform morphology is beneficial for LED applications.^{8,11,25} A 7 nm-thick Bphen layer and a 100 nm-thick Al electrode were sequentially thermally evaporated at a rate of 0.05 nm s^{-1} through a shadow mask under 1.5×10^{-6} Torr. The device area was 0.03 cm^2 as defined by the overlapping area of the ITO and Al electrodes. Fig. 2(c) also depicts the flat-band energy-level diagram of the fabricated 2D PeLED. The valence and conduction band edges of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite are -6.1 eV and -3.8 eV , respectively, obtained from ultraviolet photoelectron spectroscopy (UPS) and UV absorption measurements.

Fig. 3(a) shows the room temperature EL spectrum of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ -based PeLED. The EL spectrum peaks at 526 nm with a narrow FWHM of 15 nm, which is consistent with the PL spectrum of the pristine 2D perovskite film (Fig. 1(c)), suggesting that the EL emission of the devices results from the excitonic emission of the 2D perovskite. As shown in Fig. 3(b), the PeLED device is turned on at 2.8 V, and a luminance of $\sim 9 \text{ cd m}^{-2}$ was achieved under a driving voltage of 5 V. The EQE of the green-emitting device (see Fig. 3(c)) exhibits a rapid initial rise with increasing current density, subsequently being close to saturation after the current density is greater than 150 mA cm^{-2} . A maximum EQE of 0.005% at the current density of 200 mA cm^{-2} is obtained in the 2D $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite based LED. We note that the device stability is poor, with a lifetime of only ~ 1 min. The stability is an important topic in perovskite LEDs and efforts should be made to improve it.

We believe that the low EQE presented in the 2D PeLED can be originated from several reasons. First, the current device structure is not optimized yet, and the charge carrier can not well confined in the emission layer, as

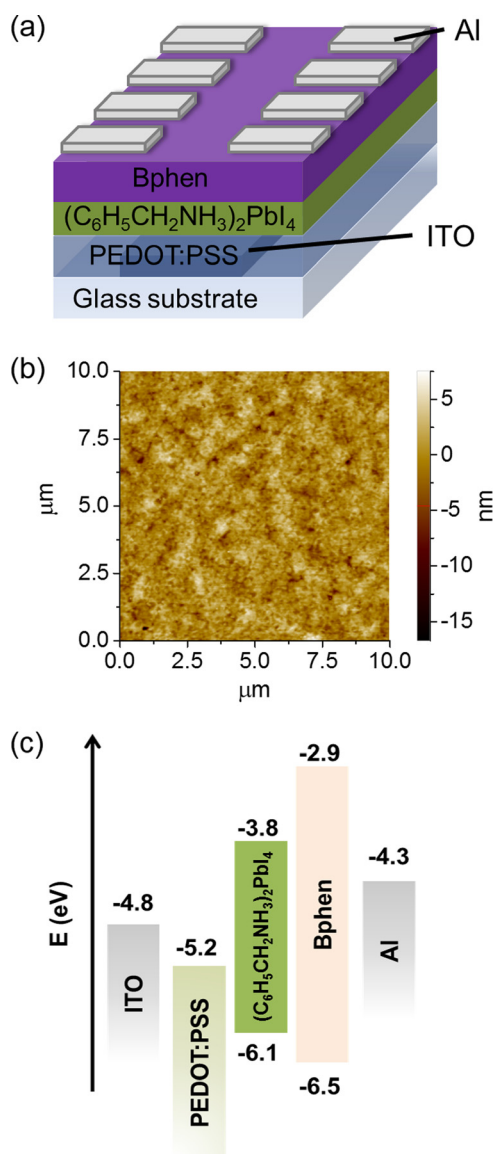


FIG. 2. (a) Device architecture of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ PeLEDs. (b) AFM image of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ perovskite film spin-coated on a PEDOT:PSS/ITO substrate. (c) Flat-band energy-level diagram of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ PeLEDs.

shown in Fig. 2(b). This would be improved by carefully screening charge transport layers and tuning interfacial energy levels.²⁵ Second, the room temperature PLQE of the 2D perovskites is low ($\sim 0.5\%$). It is necessary to overcome these two issues in next step in order to improve the device performance. Moreover, the preferred orientation of perovskite films would likely be disadvantageous for charge injection and transportation in LED devices. One can use conjugated organic cation to increase the charge transport between the layers or tune the layer alignment to vertical direction to the substrate during the film preparation process.²⁶

In summary, we have demonstrated room temperature green light-emitting diodes based on a 2D layered perovskite $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$. A maximum luminance of $\sim 9 \text{ cd m}^{-2}$ at the driving voltage of 5 V and an EQE of $\sim 0.005\%$ are achieved with the 2D PeLED. Femtosecond PL decay trace revealed that a short exciton lifetime of the

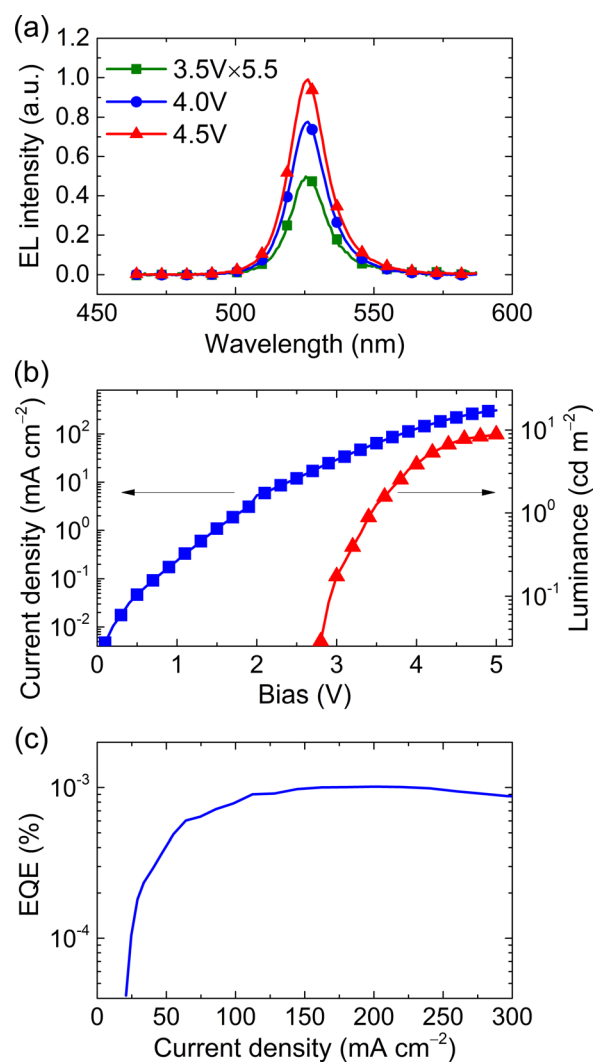


FIG. 3. (a) EL spectrum of the $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ PeLED under 3.5 V ($\times 5.5$), 4 V and 4.5 V. (b) Current density (J) and luminance versus voltage (V) of the PeLED. (c) EQE versus J of the PeLED.

$(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbI}_4$ film assumes the main responsibility for the low luminescence efficiency.

See [supplementary material](#) for the excitation intensity dependent photoluminescence quantum efficiencies (Fig. S1) and temperature dependent photoluminescence spectra of the studied 2D perovskites (Fig. S2).

This work was financially supported by the Fundamental Studies of Perovskite Solar Cells (2015CB932200), Jiangsu Natural Science Foundation (BK20131413, BK20140952), Jiangsu Specially Appointed Professor program, National Natural Science Foundation of China (61405091 and 11474164), China Postdoctoral Science Foundation, and the Synergetic Innovation Center for Organic Electronics and Information Displays. We thank Professor Peng Wang (Zhejiang University) for the help of PL lifetime measurement.

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