

Electronic Supplementary Information

Highly efficient warm white light emission in Sb³⁺-doped (NH₄)₄CdCl₆ metal halides by A-site Rb-alloying regulation

Yilin Gao, Qilin Wei, Tong Chang, Miao Ren, Yunfeng Lou, Zhengjie Tian, Yue Fan, Jiandong Yao, Bingsuo Zou, and Ruosheng Zeng*

School of Physical Science and Technology, State Key Laboratory of Featured Metal Materials and Life-cycle Safety for Composite Structures, Guangxi University, Nanning 530004, China

Corresponding author: zengrsh@guet.edu.cn

EXPERIMENTAL METHOD AND CHARACTERIZATION

Materials and Chemicals

Ammonium chloride (NH₄Cl, AR, 99.5%, Aladdin), Rubidium carbonate (Rb₂CO₃, 99.99%, Macklin), Cadmium chloride (CdCl₂, 99%, Macklin), Antimony acetate (Sb(CH₃COO)₃, 99.9%, Macklin) were purchase from Shanghai Fengzhun Biotechnology Co., Ltd. Hydrochloric acid (HCl, 37 wt% in water) and Ethanol (CH₃CH₂OH, 99.9%) were purchased from Nanning Blue Sky Experimental Equipment Co., Ltd. The chemicals and reagents needed for the experiment have not been further purified.

Synthesis of x%Sb³⁺:(NH₄)₄CdCl₆ with a variety of Sb doping concentration (x = 0, 5, 10, 15, 20, 25, and 30)

x%Sb³⁺:(NH₄)₄CdCl₆ were synthesized by a solvothermal method. First, 4mmol NH₄Cl, 1mmol CdCl₂, x mmol Sb(CH₃COO)₃, and 2 mL hydrochloric acid solution were added to Teflon autoclave (25 mL). Secondly, the mixed solution is placed in an oven at 160 °C for a reaction for 4 hours, and then the solution is slowly cooled to room temperature (RT). Ultimately, the powder sample was washed with ethanol three times and dried in a drying oven at 65°C for 4h.

Synthesis of 20%Sb³⁺:(NH₄)_xRb_{4-x}CdCl₆

The experimental synthesis method of $20\%Sb^{3+}:(NH_4)_xRb_{4-x}CdCl_6$ sample is consistent with the synthesis scheme of $20\%Sb^{3+}:(NH_4)_4CdCl_6$. However, the feeding ratio of NH_4Cl and $RbCO_3$ is adjusted, when the total amount of NH_4Cl and $RbCO_3$ is 4 mmol.

Fabrication of LED devices

LED device was prepared by NUV-LED chip (365nm). First, the $20\%Sb^{3+}:(NH_4)_xRb_{4-x}CdCl_6$ sample was thoroughly mixed with epoxy resin. and secondly, the mixture was evenly spread on the surface of the LED chip. Finally, the chip was placed in a 65 °C oven for 72 h to obtain the device.

Characterizations

The powder X-ray diffraction pattern was measured using a Cu K α ($\lambda = 0.71073 \text{ \AA}$) radiation rotating anode and an X-ray diffractometer (model: SMARTLAB 3 KW) manufactured by Rigaku Corporation in the 2θ range of 10° – 65° . The absorption spectrum of the sample powder was collected with a UV-VIS-NIR spectrophotometer (PerkinElmer Instruments, Lambda 750). The morphology of the powder was observed by scanning electron microscope ((SEM, Zeiss Sigma 500). Elemental composition and distribution are tested by an energy spectrometer (EDS, Oxford X-max20). The photoluminescence spectra, photoexcitation spectra, photoluminescence quantum yield (PLQY), and temperature-dependent photoluminescence spectrum were measured by Horiba Jobin Yvon Fluorolog-3 spectrometer. Time-resolved spectra were acquired with an Edinburgh FLS 1000 fluorescence spectrometer. Thermogravimetric analysis was performed on SHIMADZU DTG-60H at a rate of $10^\circ C/min$ from room temperature to $900^\circ C$ under nitrogen protection. The performance of LED devices is characterized by a white light LED inspection system.

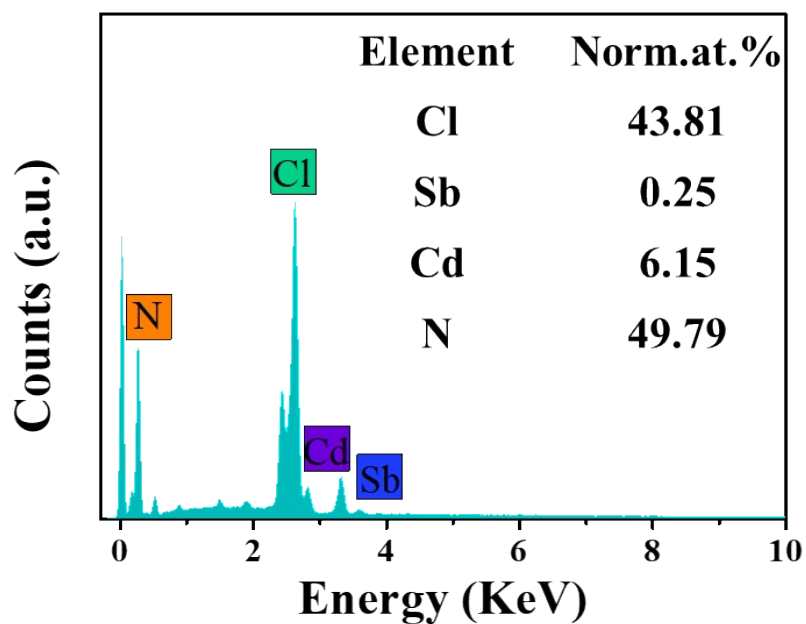


Fig. S1. X-ray energy dispersive spectra of 20% $\text{Sb}^{3+}:(\text{NH}_4)_4\text{CdCl}_6$.

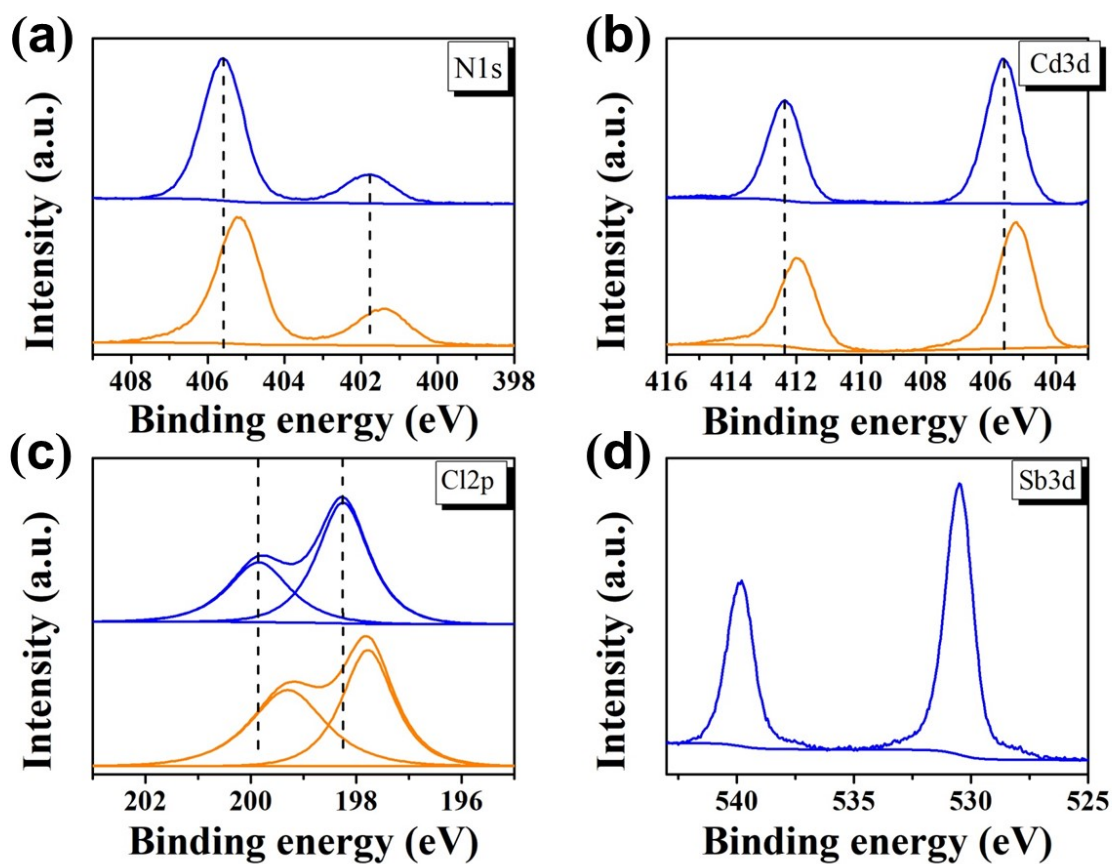


Fig. S2. High-resolution XPS spectra of N 1s, Cd 3d, Cl 2p and Sb 3d of $(\text{NH}_4)_4\text{CdCl}_6$ (blue) and 20% $\text{Sb}^{3+}:(\text{NH}_4)_4\text{CdCl}_6$ (orange), respectively.

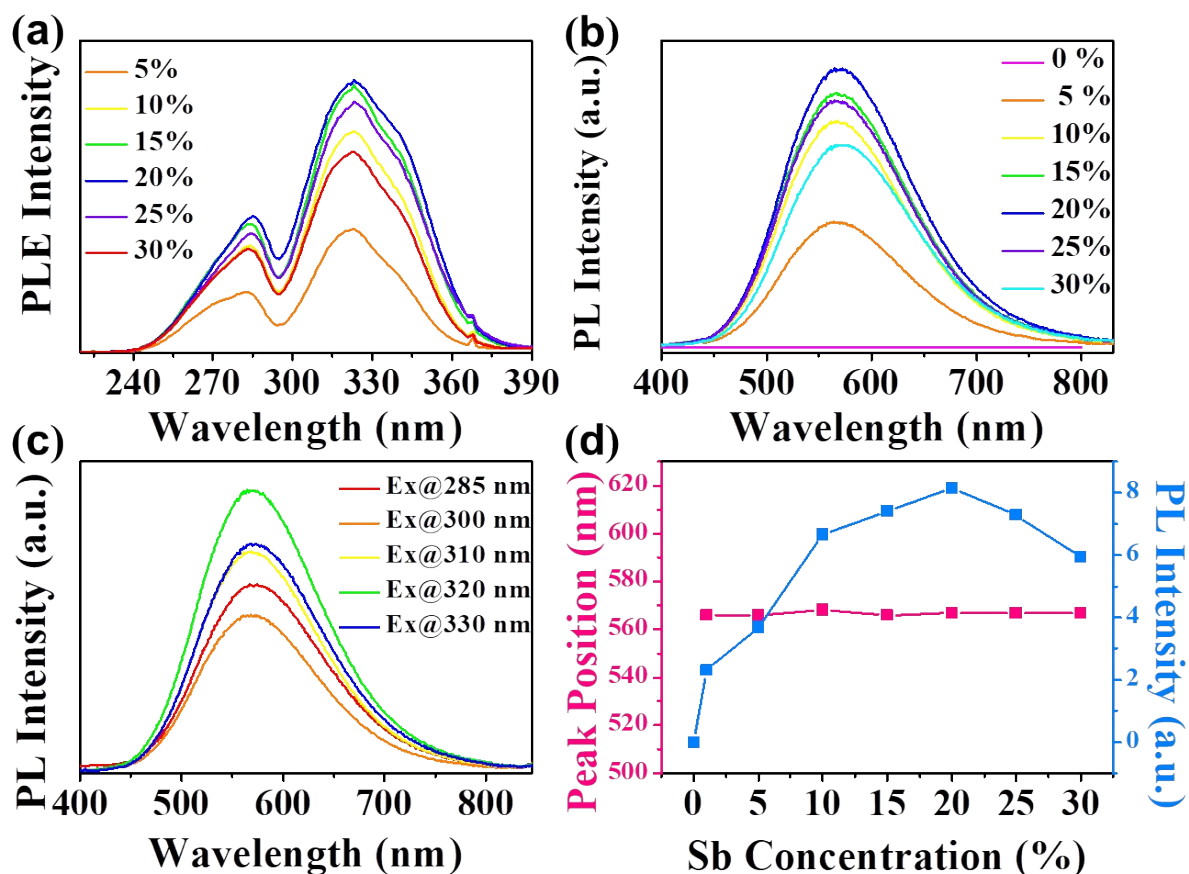


Fig. S3. (a) Normalized PLE spectra of $x\%Sb^{3+}:(NH_4)_4CdCl_6$ ($\lambda_{em} = 570$ nm). (b) PL spectra of $x\%Sb^{3+}:(NH_4)_4CdCl_6$ ($\lambda_{ex} = 320$ nm). (c) PL spectra of $20\%Sb^{3+}:(NH_4)_4CdCl_6$ samples at different excitation peaks. (d) The relationship between the doping concentration of Sb^{3+} and the change of $x\%Sb^{3+}:(NH_4)_4CdCl_6$ peak position and PL intensity, respectively.

Table S1. PL lifetime data of $x\%Sb^{3+}:(NH_4)_4CdCl_6$ ($x = 5-30$).

x	$A_1(\%)$	$\tau_1(\mu s)$	$A_2(\%)$	$\tau_2(\mu s)$	$\tau_{ave}(\mu s)$
5	99.73	2.36	0.27	12.76	2.51
10	99.71	2.69	0.28	21.60	2.55
15	99.79	2.61	0.20	17.10	2.79
20	99.77	2.63	0.22	16.31	2.82
25	99.65	2.39	0.34	11.18	2.53
30	99.72	2.18	0.27	10.90	2.29

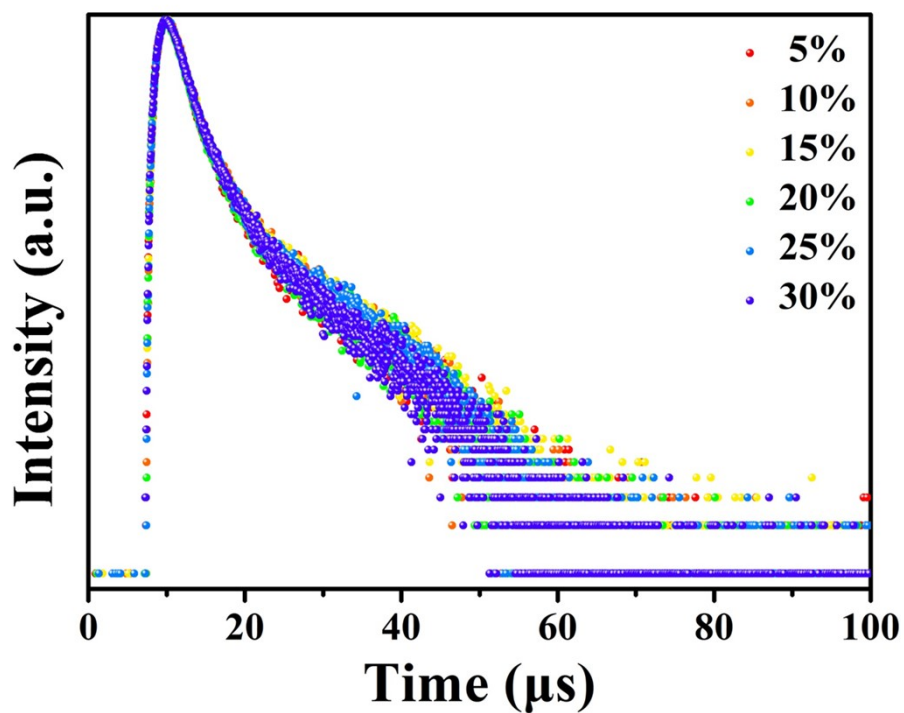


Fig. S4. PL decay of $x\% \text{Sb}^{3+}:(\text{NH}_4)_4\text{CdCl}_6$ ($x = 5\text{--}30$) samples excited under 320 nm excitation at the emission of 570 nm.

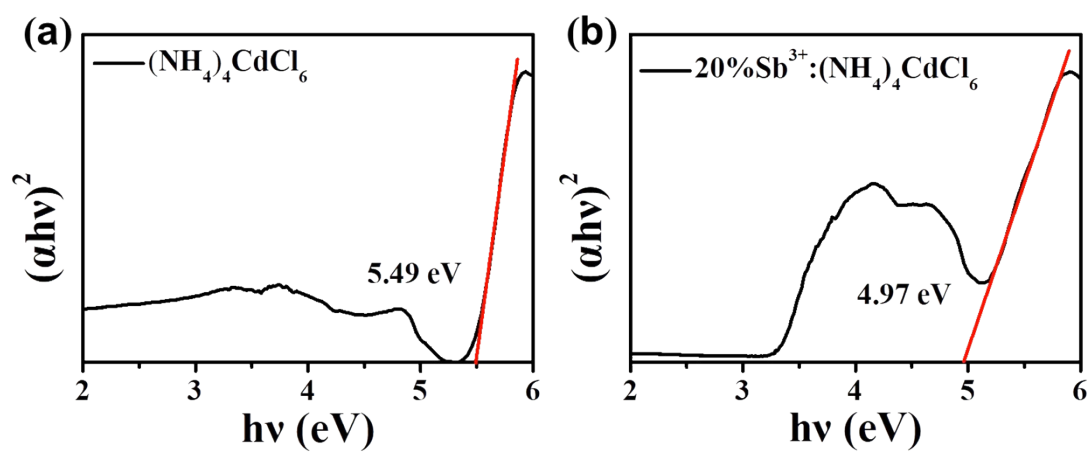


Fig. S5. The Tauc plots of $(\text{NH}_4)_4\text{CdCl}_6$ and $20\% \text{Sb}^{3+}:(\text{NH}_4)_4\text{CdCl}_6$, respectively.

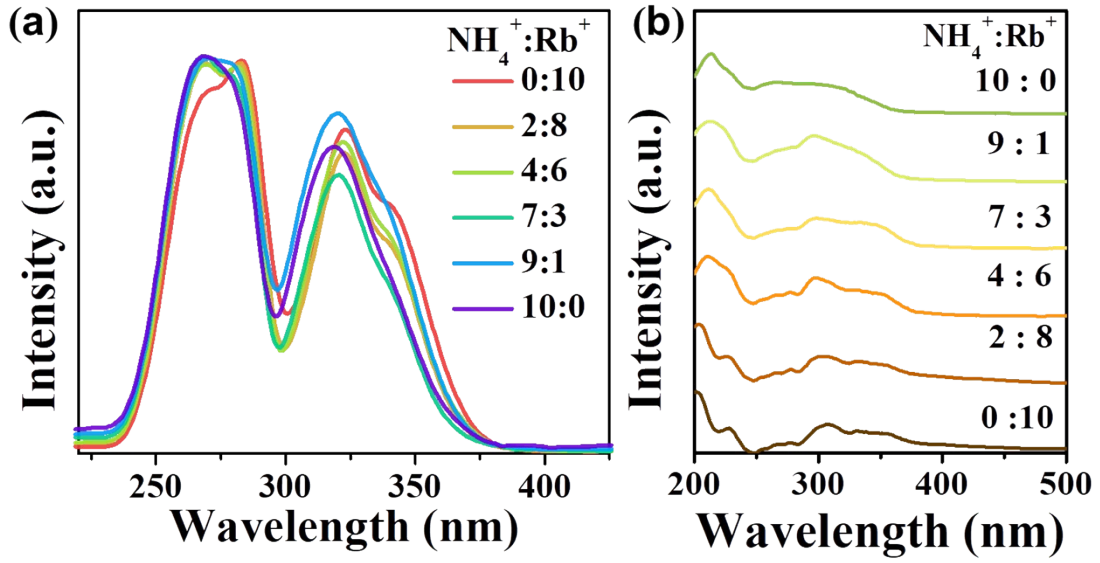


Fig. S6. (a) The PLE spectra of 20% $\text{Sb}^{3+}:(\text{NH}_4)_x\text{Rb}_{4-x}\text{CdCl}_6$. (b) The absorption spectra of 20% $\text{Sb}^{3+}:(\text{NH}_4)_x\text{Rb}_{4-x}\text{CdCl}_6$ ($x = 4, 3.2, 2.8, 1.6, 0.4, 0$).

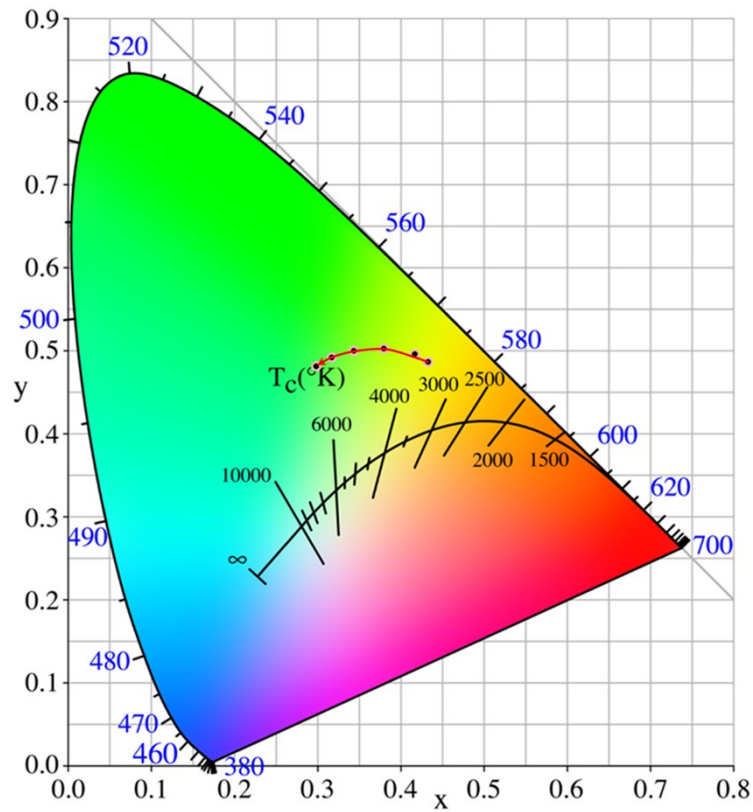


Fig. S7. CIE of the corresponding samples with different Rb^+ concentrations calculated by CIE1931.

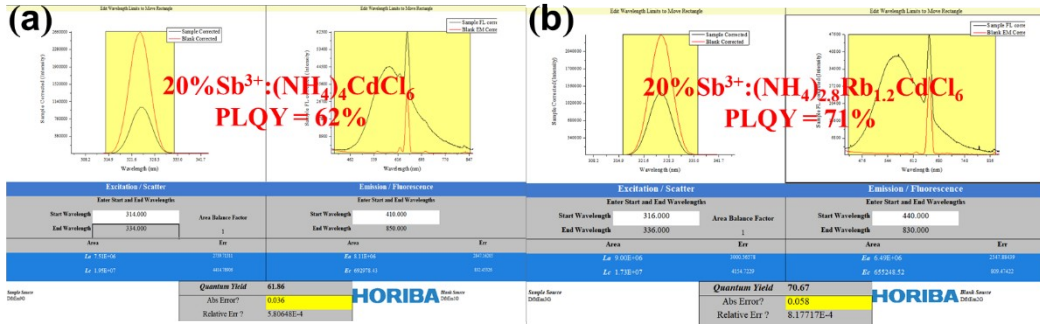


Fig. S8. The PLQYs of (a) 20%Sb³⁺:(NH₄)₄CdCl₆ and (b) 20%Sb³⁺:(NH₄)_{2.8}Rb_{1.2}CdCl₆, respectively.

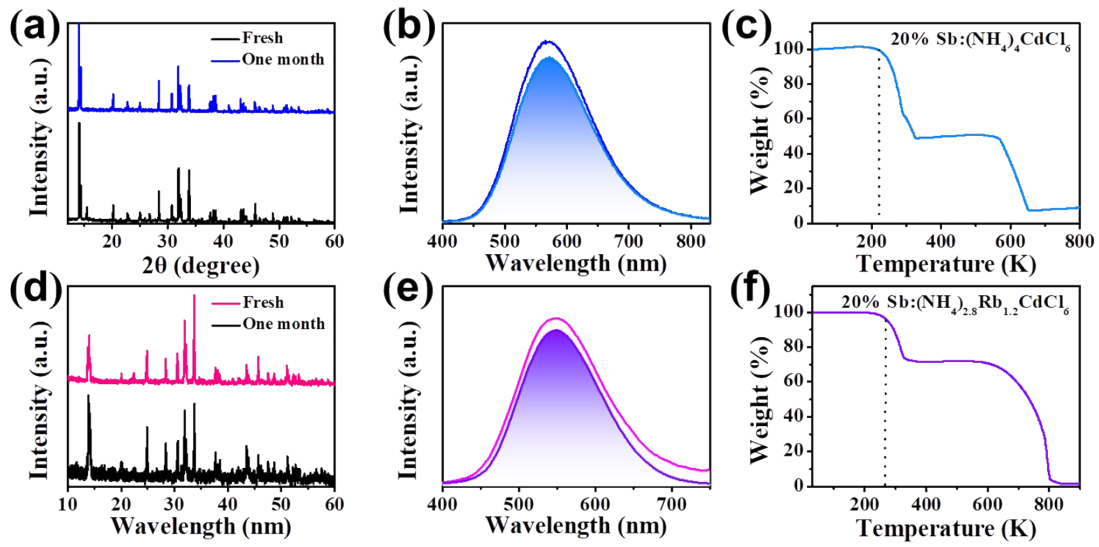


Fig. S9. Comparison of X-ray diffraction patterns (a), PL spectra (b) and thermogravimetric analysis (c) of 20%Sb³⁺:(NH₄)₄CdCl₆ fresh and one month later samples, respectively. (d-e) Comparison of X-ray diffraction patterns (d), PL spectra (e) and thermogravimetric analysis (f) of 20%Sb³⁺:(NH₄)_{2.8}Rb_{1.2}CdCl₆ fresh and one month later samples, respectively.

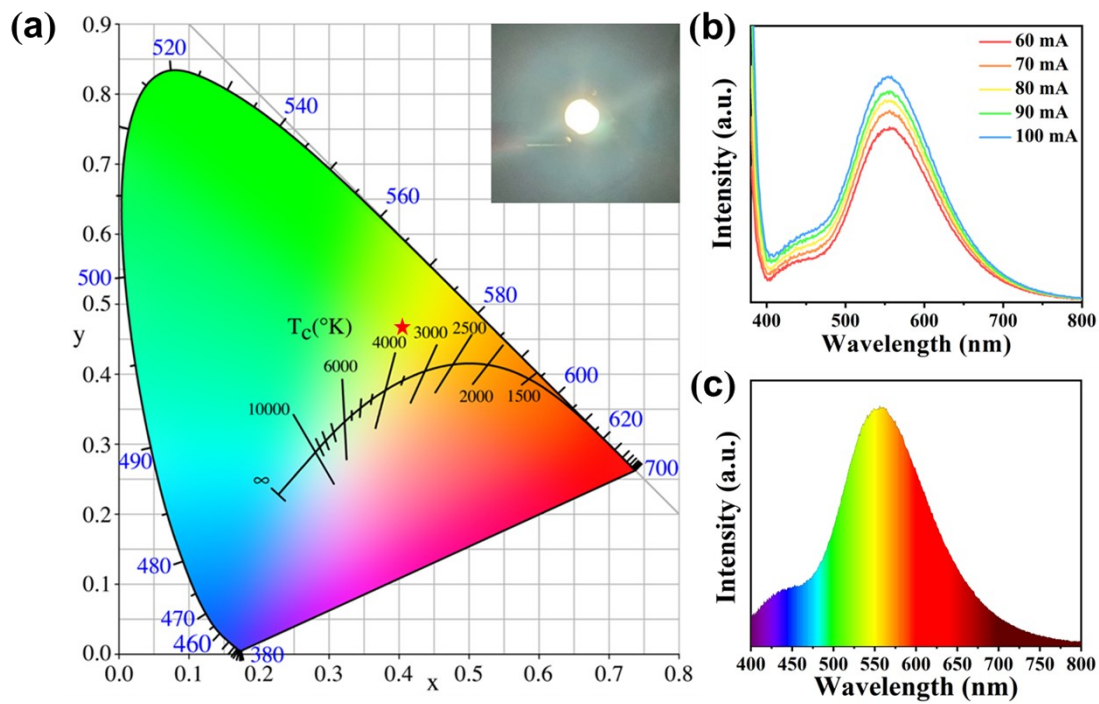


Fig. S10. (a) CIE coordinates corresponding to the emission of 20% $\text{Sb}^{3+}:(\text{NH}_4)_{2.8}\text{Rb}_{1.2}\text{CdCl}_6$, and the illustration is a picture of WLED working at 3.5V using ultraviolet chip $\lambda_{\text{ex}}=365$ nm. (b) PL spectra of devices driven by different currents. (c) Electroluminescent spectra of the NUV-pumped WLED.