

Supporting Information

Dual near infrared emission in Ag₂Se quantum dots via Pb doping for broadband mini light-emitting diodes

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Experimental methods

Chemicals

Selenium powder (Se, 99.9%), 1-octadecene (ODE, 90%), tributyl phosphine (TBP, 98%) and tetrachloroethylene (C_2Cl_4 , 98%) were purchased from Macklin Biochemical. Silver acetate (AgAc, 99.5%), lead acetate trihydrate ($Pb(Ac)_2 \cdot 3H_2O$, 99%), toluene ($C_6H_5CH_3$, 99.5%) and 1-dodecanethiol (DT, 98%) were bought from Sigma-Aldrich. Methyl alcohol (CH_3OH , 99.8%) and acetone (C_3H_6O , 99%) were obtained from Sinopharm Chemical Reagent. All of the above reagents were employed to prepare pure Ag_2Se QDs and Pb doped Ag_2Se QDs. The composites including polydimethylsiloxane (PDMS, Dow Corning), polyvinyl pyrrolidone (PVP, Macklin) and polymethyl methacrylate (PMMA, Macklin) and tetraethyl orthosilicate (TEOS, Aladdin) were purchased for fabricating QDs converted LED. InGaN blue emitting LEDs (emission at 450 nm, the operating voltage (6.0 V-8.0 V) were purchased from Shenzhen Looking Long Technology Corporation. All the chemical reagents were purchased and used without further purification.

Preparation

Synthesis of Ag_2Se QDs

The Ag_2Se QDs were prepared by a facile hydrothermal method. Briefly, 0.3 g of Se powder and 2 mL of TBP solution were added into a three necked flask. Se powder was dispersed uniformly and reacted fully in TBP solution by ultrasound for 10 min and stirring at 850 r/min for 90 min. The obtained TBP-Se solution was employed for later. Then, 0.550 g of AgAc was added into a single necked flask containing 40 mL

of DT and 60 mL of ODE. The mixture was stirred by magnetic stirring apparatus at 900 r/min at 160 °C. Subsequently, the pre-synthesized TBP-Se solution was added into the mixed solution, and stirred continuously at 900 r/min at 160 °C for 45 min to make the adequate growth of nanocrystals. Afterwards, the solution containing QDs was cooled naturally to room temperature. The solution was washed three times by acetone solution in order to remove any possible remnants, and centrifuged for 7 min to precipitate the QDs. Finally, the QDs powder was dried in oven at 60 °C for 5 h for further doping Pb ions subsequently. The entire reaction process was carried out under argon atmosphere away from light.

Synthesis of Pb doped Ag₂Se QDs

0.19 g of Pb(Ac)₂·3H₂O was added into 40 mL of CH₃OH in the three-necked flask, and ultrasonic-dispersed for 10 min. And the solution reacted fully in an electric heating mantle at 37 °C for 60 min. The obtained lead precursor solution was used for later. To obtain different concentration of Pb doped Ag₂Se QDs, the dried Ag₂Se QDs powders in the first step were divided with 12 portions for 0.02 g each, and added individually into C₆H₅CH₃ and DT mixture. Then, 0, 0.05 mL, 0.13 mL, 0.25 mL, 0.35 mL, 0.50 mL, 0.60 mL, 0.65 mL, 0.75 mL, 0.85 mL, 0.90 mL, 1.10 mL of the pre-synthesized Pb precursor solutions were added separately into the mixture solution, and heated at 60 °C for 10 min. Finally, Pb doped Ag₂Se QDs solutions were obtained, respectively, with 0, 0.46 mol%, 1.15 mol%, 2.30 mol%, 3.22 mol%, 4.60 mol%, 5.52 mol%, 5.98 mol%, 6.90 mol%, 7.82 mol%, 8.28 mol%, 10.12 mol% of Pb doping. These Pb doped Ag₂Se QDs were washed three times with ethanol,

centrifuged at 12000 rpm for 7 min and then dried in an oven at 60 °C for 6 h. The whole reaction process was carried out in an argon environment and protected from light.

Fabrication of NIR QDs converted LED devices

A schematic of the fabricated NIR QDs converted LED device was shown in Fig. S9. First, Pb doped Ag₂Se QDs-PMMA composite film was prepared as follows. 1.50 g of PMMA was firstly dissolved in 4.50 mL of chloroform, and stirred at room temperature for 30 min. Pb doped Ag₂Se QDs were added into the mixed solution, and stirred for 1 h at the room temperature. Subsequently, 750 μL of the obtained QDs-PMMA mixture solution was dripped on the surface of glass slide, and dried immediately for 12 h in a vacuum drying oven. In the work, an inorganic passivation layer of PVP/silica was further dip-coated on the QDs-PMMA film to prevent the diffusion of the oxygen molecules. The preparation process comprises the following steps: 2.50 g of PVP was dissolved in 6 mL of ethanol, and stirred at room temperature for 45 min. 400 μL of the above mixture was dripped on the surface of QDs-PMMA film, and dried in a vacuum drying oven at the room temperature for 45 min. The QDs-PMMA-PVP film was obtained. 1 mL of TEOS solution was further coated on the surface of the obtained QDs-PMMA-PVP film. The QDs-PMMA-PVP-silica film was finally detached from the surface of glass slide, and cured thermally on InGaN LED chip by PDMS curing agent. Finally, the NIR QDs converted LED device was dried in a vacuum drying oven at 40 °C for 8 h for characterization later.

Characterization

For morphological characterizations, the prepared QDs samples were dissolved and ultrasound-dispersed in tetrachloroethylene solution, and then dropped in carbon films and dried for 12 h at room temperature. The morphologies of the prepared QDs samples were observed via transmission electron microscopy (TEM, HITACHI HT7700, Japan) at an acceleration voltage of 5 kV. High resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) were conducted using a JEOL JEM-2100F microscope (JEOL, Tokyo, Japan) with an acceleration voltage of 200 kV. For measuring optical properties, the QDs powders were dissolved and dispersed uniformly in tetrachloroethylene solution. Absorption spectra were recorded on an ultraviolet-visible (UV) spectrophotometer (UV-2600, Shimadzu, Japan) with the scanning range from 200 nm to 800 nm. NIR emission spectra and fluorescence lifetimes were performed by fluorescence spectrometer (Edinburgh FLS-1000, Edinburgh Instruments, UK) equipped with a liquid nitrogen-cooled photomultiplier (Hamamatsu R5509-72, Hamamatsu, Japan) under xenon lamp 470 nm and 808 nm laser diode excitation, respectively. For structural characterizations, the crystal structures of the samples were collected on a Bruker SmartApex-II X-ray diffractometer (XRD, Bruker, Germany) using a graphite-monochromatic MoK α radiation. The scanning range of 2θ is 20° - 70° with a step length of 0.02° . The structures of the samples were further analyzed by fourier transform infrared spectrometer (FTIR, Nicolet Magna 750, USA) working in a spectral range from 400 cm^{-1} to 4000 cm^{-1} using the KBr pellet technique. Elemental chemical states of the samples were measured using an X-ray photoelectron

spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher, USA). Accurate compositions and contents of the samples were determined on an inductively coupled plasma optical emission spectrometer (ICP-OES, Thermo Fisher Scientific 7400 series, USA). The electroluminescence (EL) spectra were recorded by Ocean Optics fiber spectrometer QE65 Pro (QE65 Pro, Ocean Optics, USA) under various driven voltage. The NIR EL images of NIR QDs converted LED device were collected by InGaAs IR camera (NIRvana 640, Princeton Instruments, USA). The bioimaging for vessel and tissue were also conducted by the InGaAs IR camera under the irradiation of the fabricated NIR QDs converted LEDs. The photographs were taken by a 650 nm long pass filter.

Supporting Figures and Tables

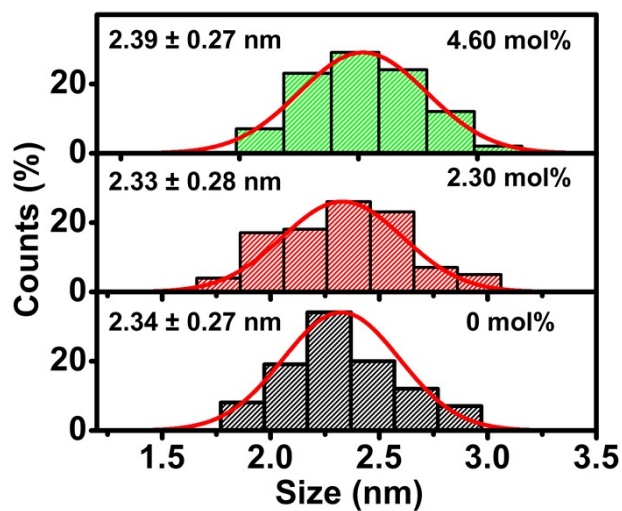


Fig. S1 The size distribution of 0 mol%, 2.30 mol% and 4.60 mol% Pb doped Ag_2Se QDs by counting 100 particles.

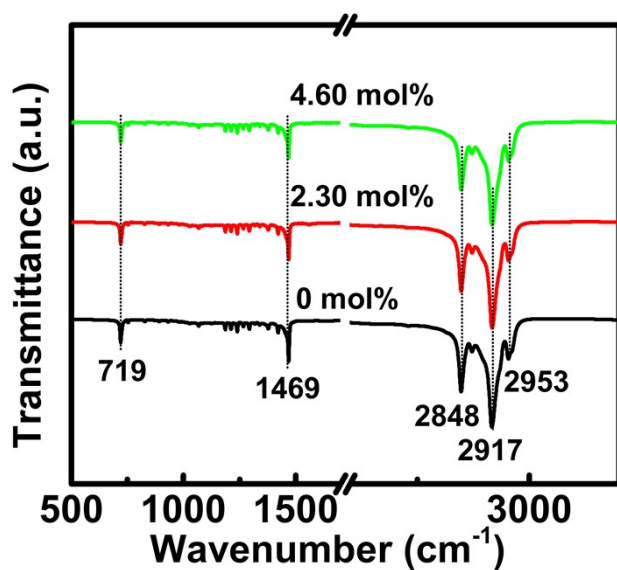


Fig. S2 FTIR spectra of 0 mol%, 2.30 mol% and 4.60 mol% Pb doped Ag_2Se QDs.

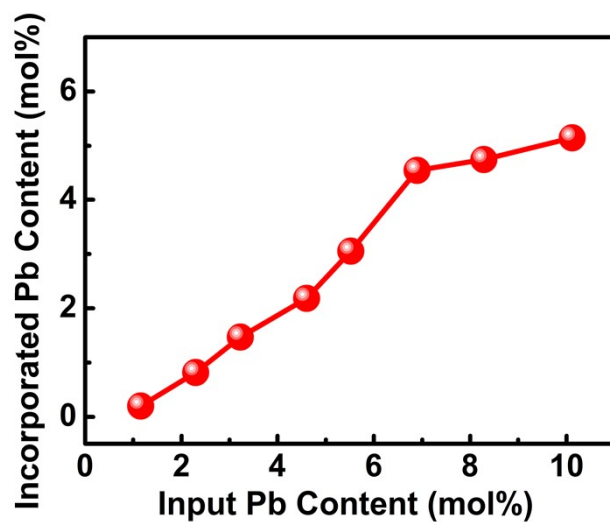


Fig. S3 Pb content of the incorporated into Ag_2Se QDs with doping Pb concentration from 1.15 mol% to 10.12 mol% by ICP-OES measurement.

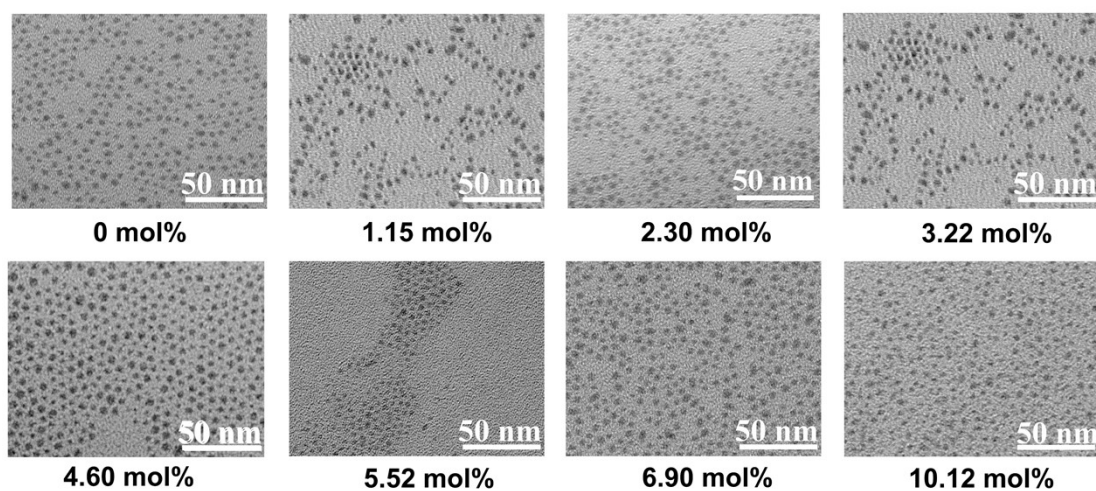


Fig. S4 TEM images of 0 mol%, 1.15 mol%, 2.30 mol%, 3.22 mol%, 4.60 mol%, 5.52 mol%, 6.90 mol% and 10.12 mol% Pb doped Ag_2Se QDs. Scale bars are 50 nm.

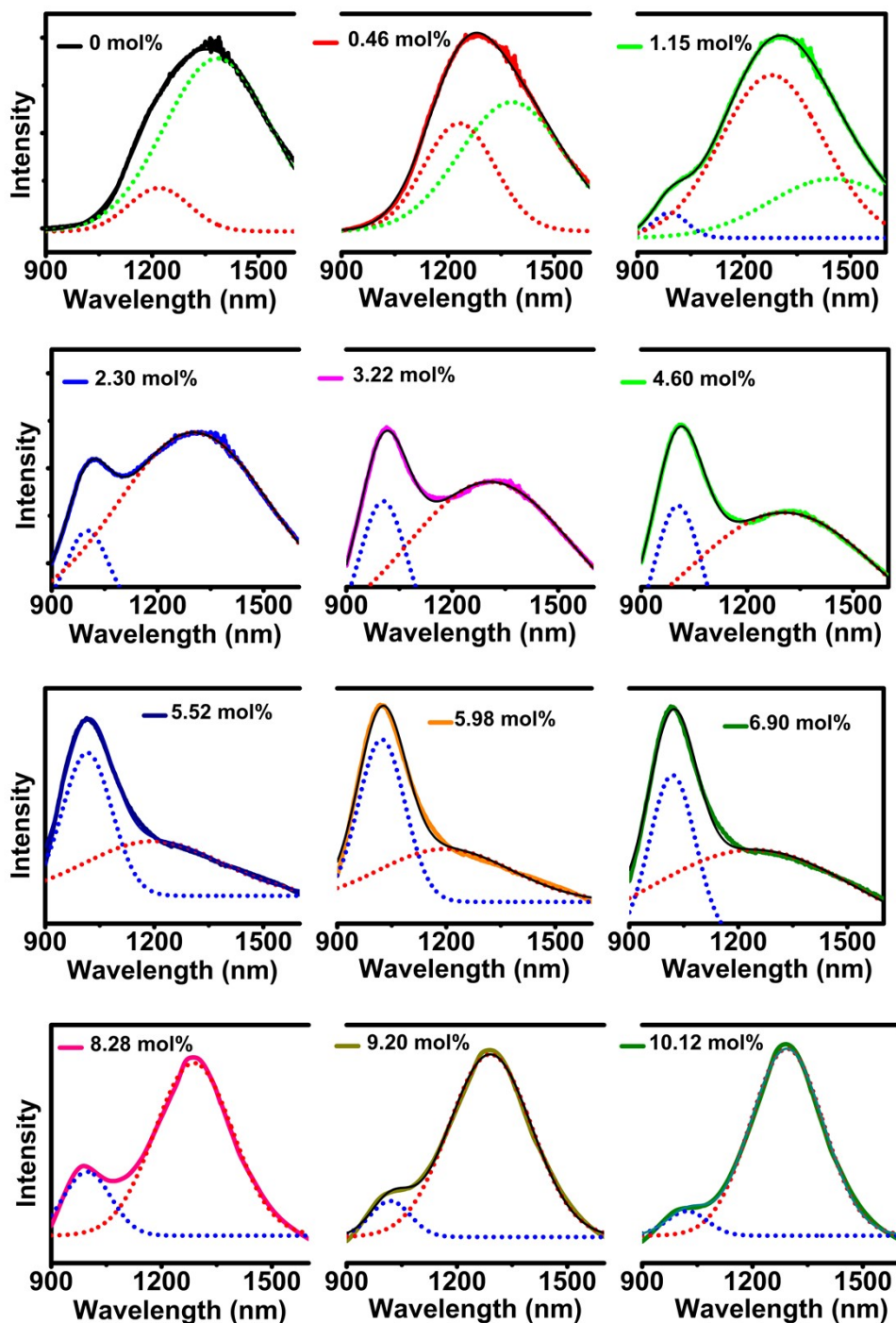


Fig. S5 The fitted NIR emission spectra of Pb doped Ag₂Se QDs with doping Pb content from 0 to 10.12 mol% by multi-Gaussian peak fitting. The experimental data are shown in colored solid lines. The dashed lines are the individual components by Gaussian fitting, and the black solid lines are the sum of individual fitting lines.

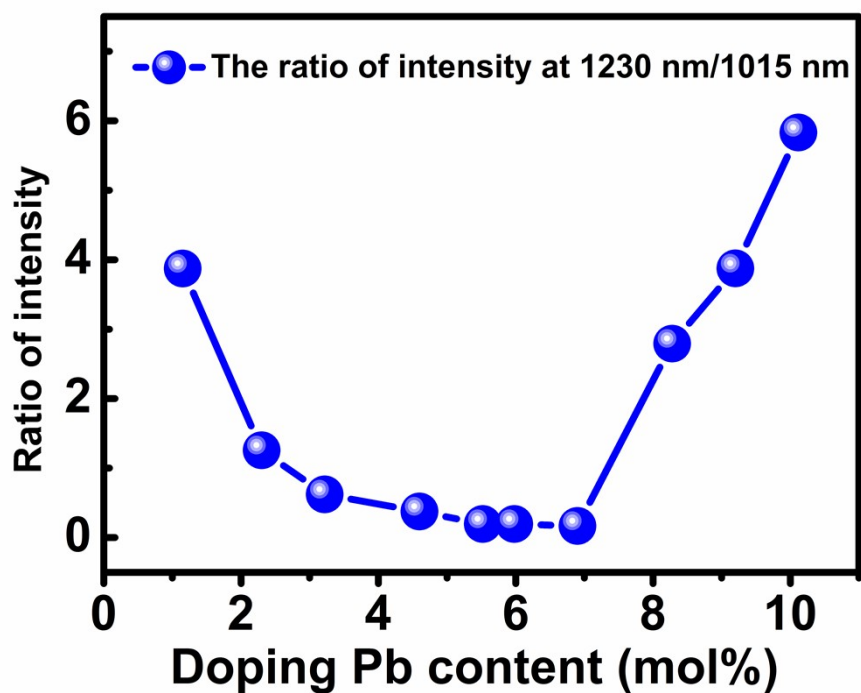


Fig. S6 The ratio of the intensity of the fitted emission peak at 1230 nm and 1015 nm.

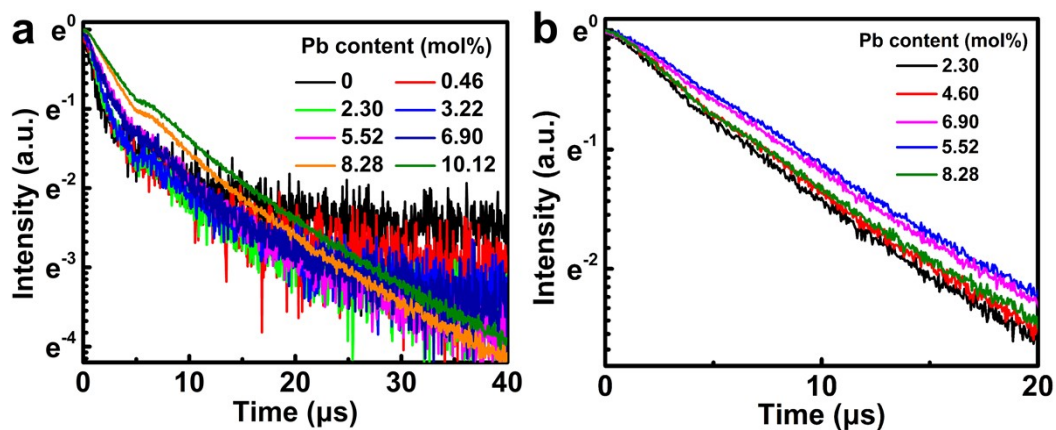


Fig. S7 Fluorescence decay curves of Pb doped Ag_2Se QDs with doping Pb concentration from 0 to 10.12 mol% monitored at (a) 1300 nm and (b) 1015 nm, respectively.

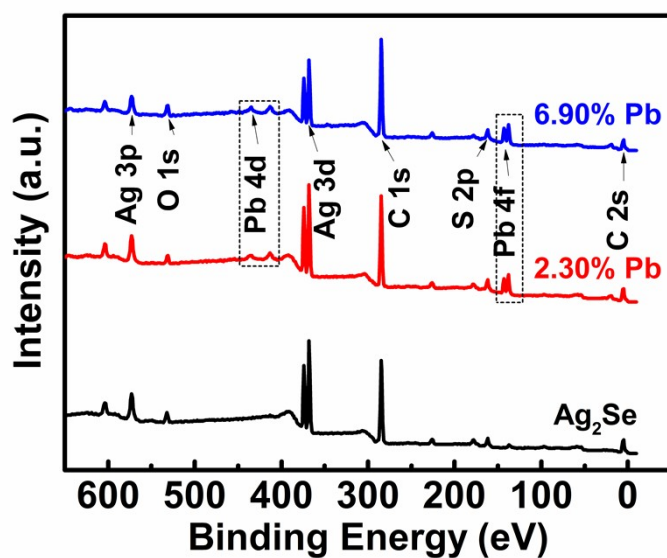


Fig. S8 XPS survey spectra of 0, 2.30 mol% and 6.90 mol% Pb doped Ag_2Se QDs.

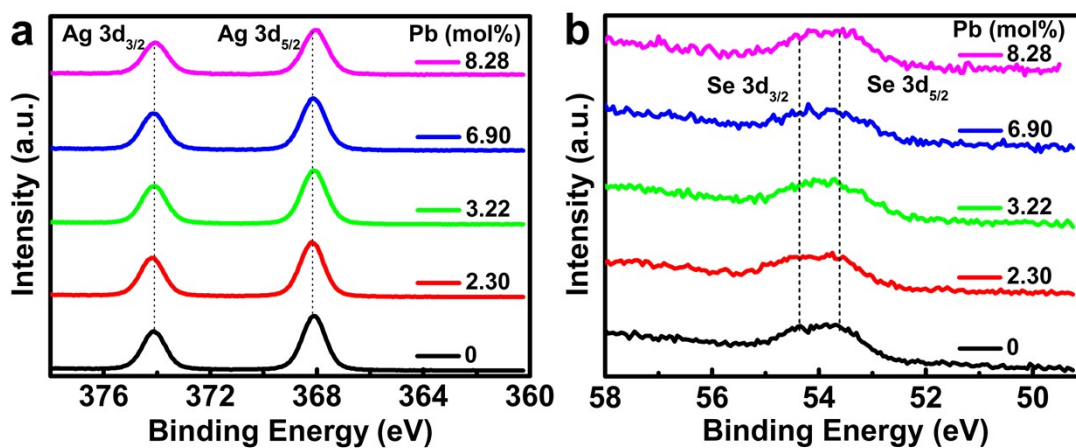


Fig. S9 XPS spectral regions of (a) Ag 3d and (b) Se 3d of 0, 2.30 mol%, 3.22 mol%, 6.90 mol% and 8.28 mol% Pb doped Ag_2Se QDs.

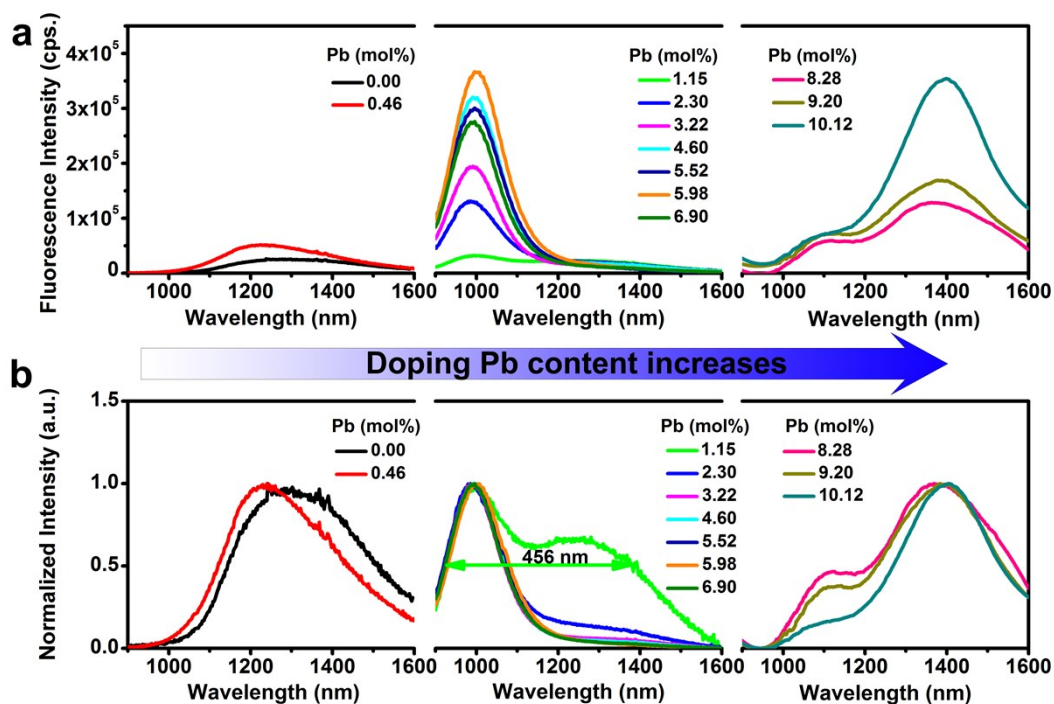


Fig. S10 (a) NIR emission spectra and (b) normalized NIR PL spectra of Pb doped Ag_2Se QDs with increasing Pb content from 0 to 10.12 mol% under 470 nm xenon lamp excitation.

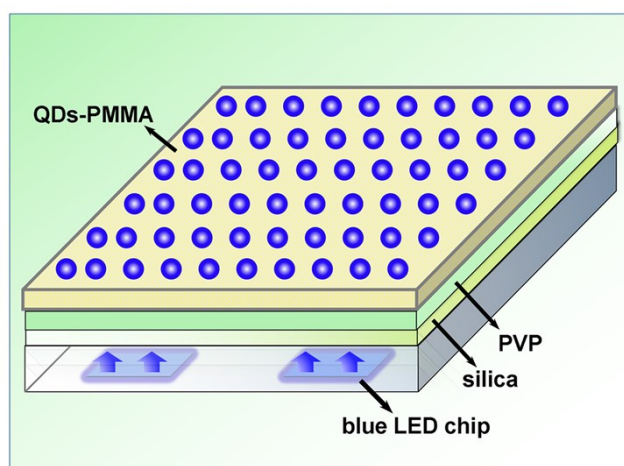


Fig. S11 A schematic diagram of the as-fabricated NIR mini-LED.

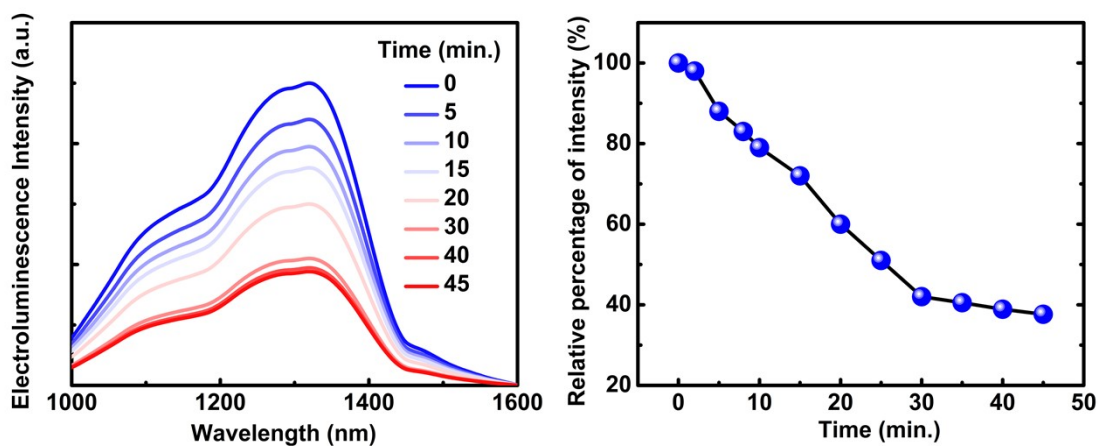


Fig. S12 (a) Time-dependent electroluminescence spectra and (b) the relative percentage of electroluminescence intensity of the fabricated 2.30 mol% Pb doped Ag_2Se QDs converted NIR mini-LED under 6.0 V driven voltage.

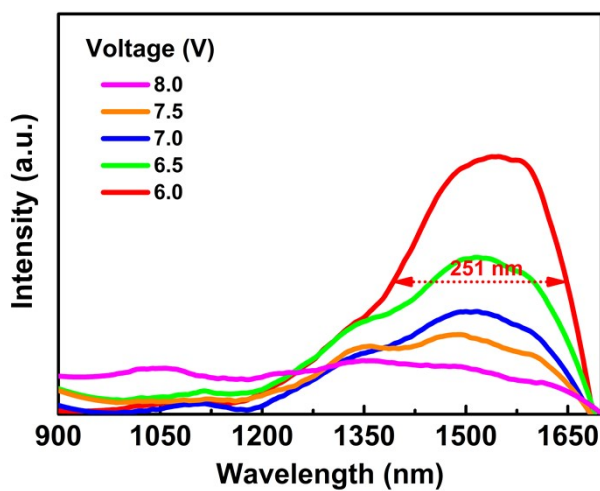


Fig. S13 Electroluminescence spectra of the pure Ag_2Se QDs converted NIR mini-LED under 6.0-8.0 V driven voltages.

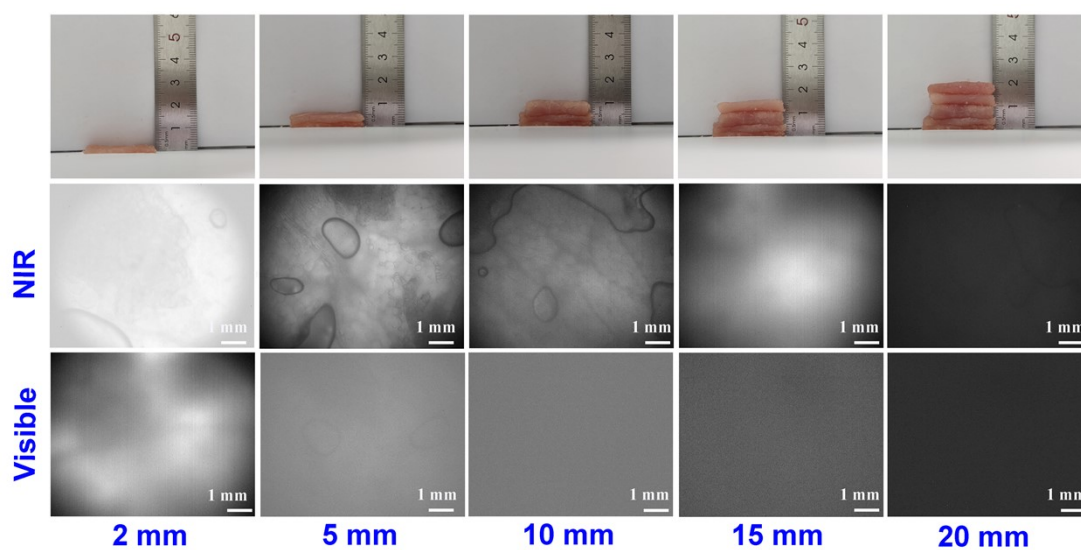


Fig. S14 Tissue penetration test of different thickness (2 mm, 5 mm, 10 mm, 15 mm and 20 mm) of pork slices under the fabricated Pb doped Ag_2Se QDs converted NIR mini-LED irradiation and conventional visible optical microscope based on the experimental set-up in the schematic diagram of Figure 4c.

Table S1. Fluorescence lifetimes τ_1 and τ_2 monitored at 1300 nm, and the lifetime τ_3 monitored at 1015 nm of Pb doped Ag_2Se QDs (0-10.12 mol%).

Pb content (mol%)	monitored at 1300 nm		monitored at 1015 nm
	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)
0	0.90	8.21	-
0.46	1.09	8.19	-
2.30	1.00	8.10	6.36
4.60	1.25	9.16	7.20
5.52	1.43	9.60	8.60
6.90	2.18	9.81	8.52
8.28	2.35	10.27	7.43
10.12	2.56	10.77	-

Table S2. The value of intrinsic bandgap and Pb dopants related energy bandgap of Pb doped Ag₂Se QDs (0-10.12 mol%).

Pb content (mol%)	Intrinsic bandgap (eV)	Pb dopants related energy (eV)
0	2.25	
0.46	2.28	
1.15	2.37	1.55
2.30	2.52	1.94
3.22	2.37	1.79
4.60	2.34	1.83
5.98	2.39	1.83
6.90	2.44	1.85
8.28	2.46	2.07
10.12	2.57	2.16