Electronic Supplementary Information

Ultra-Broadband Near-Infrared Emission $CuInS_2$/ZnS Quantum Dots with High Power Efficiency and Stability for the Theranostic Applications of Mini Light-Emitting Diodes

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Experimental

Synthesis of NIR-emitting $CuInS_2$/ZnS quantum dots (QDs)

In a typical synthesis of ternary $CuInS_2$ core QDs, 0.4 mmol of CuI (99.999%), 0.5 mmol of InI_3 (99.999%), and 1.1 mmol of elemental sulfur (99.998%) were mixed in a three-neck flask with 5 mL of oleylamine (OLA, 70%) and 1.5 mL of 1-dodecanethiol (DDT, ≥98%). The mixture was heated to 120°C during degassing and further heated under N_2 purging to a growth temperature of 220°C. The mixture was maintained at this temperature for 30 min for the growth of core QDs. Then, sequential multiple ZnS shelling on $CuInS_2$ cores was implemented as follows: the first ZnS stock solution comprising 8 mmol Zn acetate dihydrate (reagent grade) in 8 mL of oleic acid (OA, 90%) and 4 mL of 1-octadecene (ODE, 90%) was slowly introduced into the $CuInS_2$ core growth solution at 240°C for 1 h and 15 min. Then, the second ZnS stock solution prepared by dissolving 4 mmol of Zn acetate dihydrate, 4 mL of OA, 2 mL of ODE, and 2 mL of DDT was injected dropwise. The reaction was retained at 240°C, and the shelling reaction was maintained for 30 min. The last ZnS stock solution, containing 4 mmol of Zn stearate (10%-12% Zn basis), 4 mL of ODE, and 2 mL of DDT, was slowly added and reacted for 2 h at the same temperature. As-synthesized $CuInS_2$/ZnS QDs were repeatedly purified by centrifugation (9000 rpm, 10 min) with a solvent combination of hexane/ethanol and redispersed in hexane.

Material Characterization

The absorption spectra of $CuInS_2$ core and $CuInS_2$/ZnS core/shell QDs were recorded by a UV-visible–NIR absorption spectrophotometer (Shimadzu, UV-3600 Plus). A powder XRD (Rigaku, Ultima IV) with Cu K_α radiation was employed to identify core/shell heterostructure. The particle TEM image of $CuInS_2$/ZnS QDs was collected using a JEM-2100F (JEOL Ltd.) operating at 200 kV. The spectra of mini-LED packages were recorded by the LED measurement system, which is equipped with a spectroradiometer (Instrument Systems, CAS140CT-153) and integrating spheres (Instrument Systems, ISP-250). The penetration of $CuInS_2$/ZnS QD mini-LED was tested with carrier and the photomultiplier of the spectrofluorometer (Edinburgh Instruments, PMT980) with a spectral range from 185 nm to 980 nm.

Photoluminescence quantum yield

PL spectrum and quantum yield (QY) were measured by the UV–NIR absolute PL QY spectrometer (Hamamatsu Photonics, C13534), which composed of a high-power Xe lamp (Hamamatsu Photonics, L13685-01) and A13686 excitation filter. The center of excitation wavelength was set at 468 nm. As the principle, the photoluminescence quantum yield was calculated that the number of photons emitted as photoluminescence from $CuInS_2$/ZnS QDs was divided by the number of photons absorbed by $CuInS_2$/ZnS QDs.

Supplementary Figures and Tables

State of $CuInS_2$/ZnS	Center Wavelength (nm)	FWHM (nm)
dispersion	816 nm	246 nm
powder	896 nm	215 nm

Table S1 Center wavelength and full width at half maximum (FWHM) of $CuInS_2$/ZnS QDs.

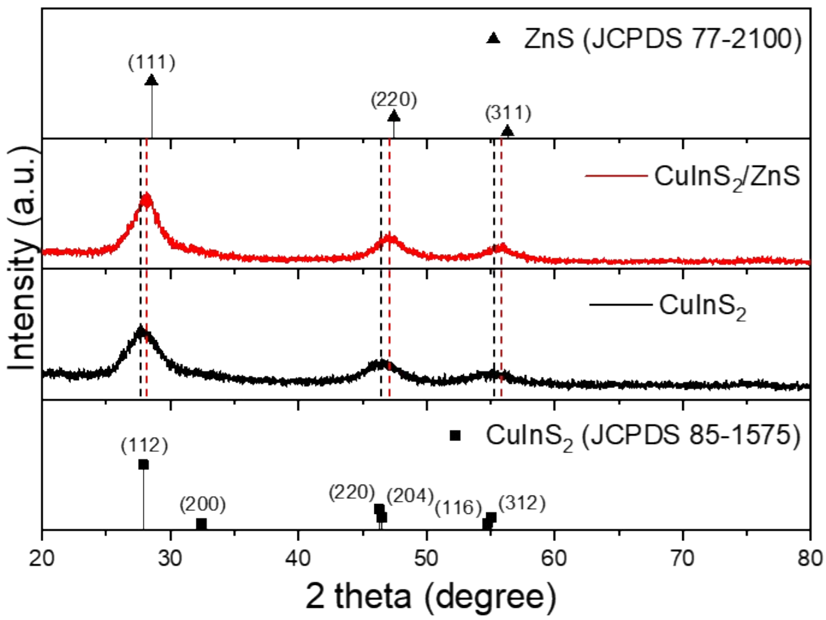

Fig. S1 Comparison of XRD patterns of $CuInS_2$ core and $CuInS_2$/ZnS core/shell QDs.

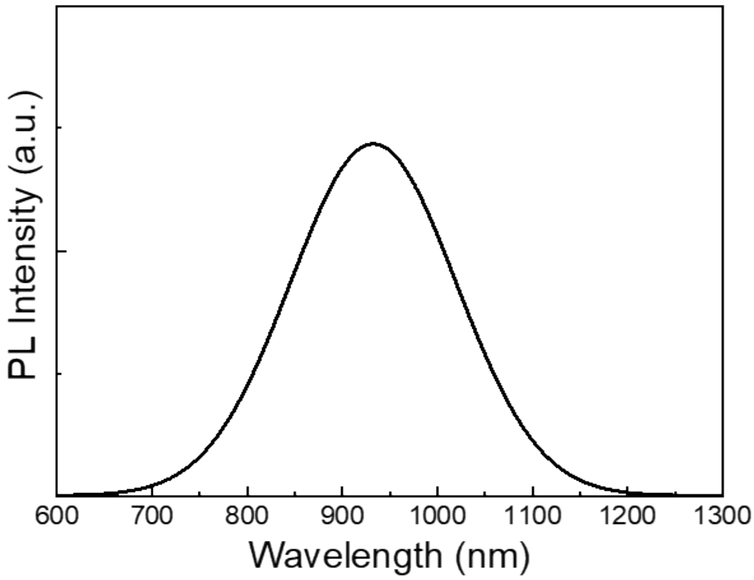

Fig. S2 PL spectrum of $CuInS_2$ core QDs peaking at 933 nm.

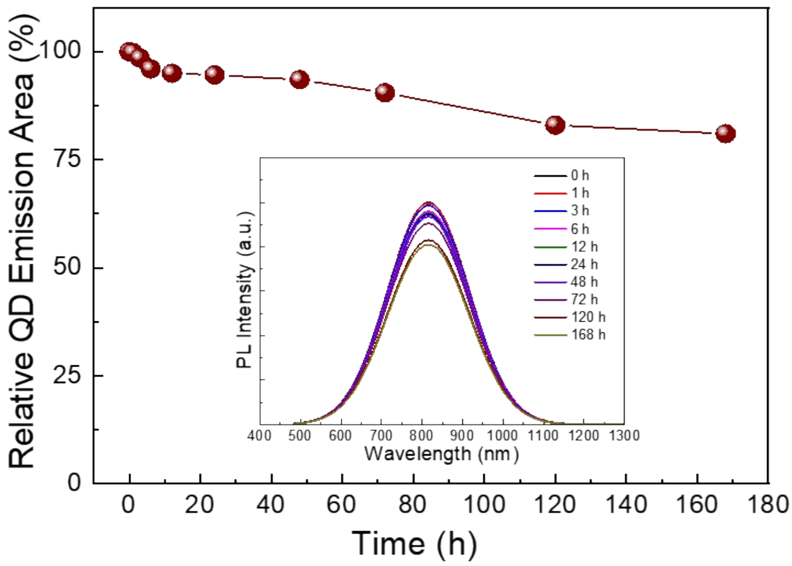

Fig. S3 Temporal change in relative emission area and corresponding PL spectra (inset) of $CuInS_2$/ZnS QDs (dispersed in hexane) under room storage for a prolonged period of time up to 168 h.

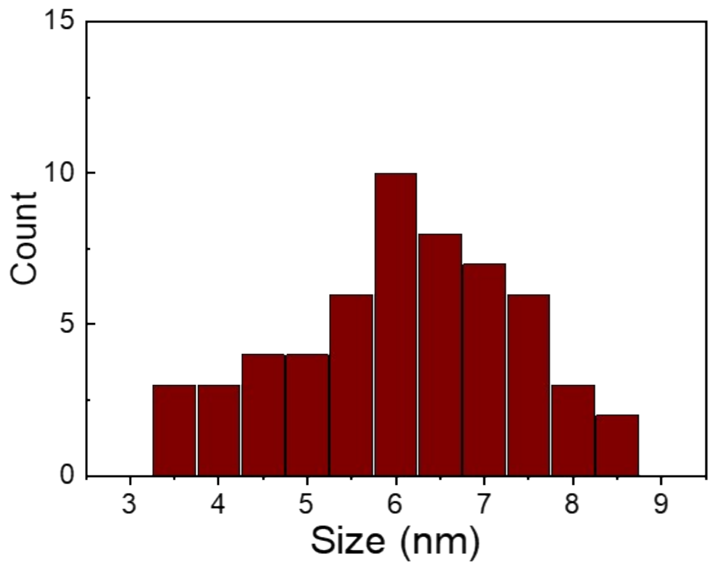

Fig. S4 TEM-based size histogram of $CuInS_2/ZnS$ QDs.

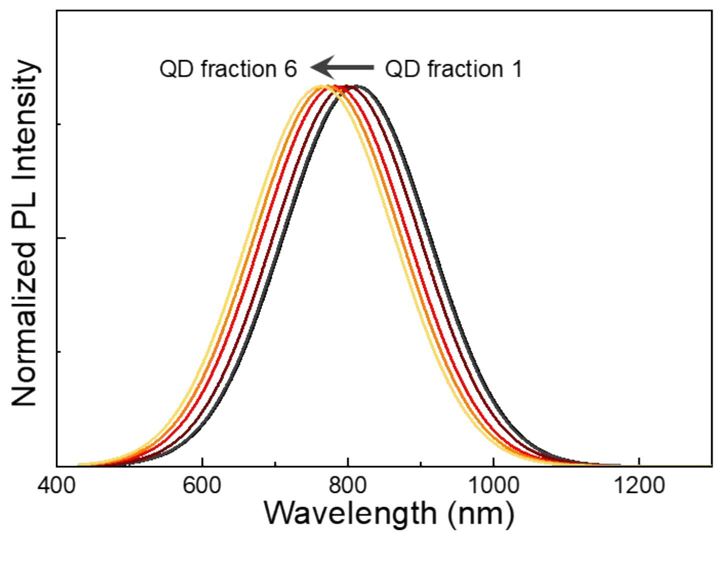

Fig. S5 Normalized PL spectra of a series of QD fractions obtained by repeated size-sorting processes.

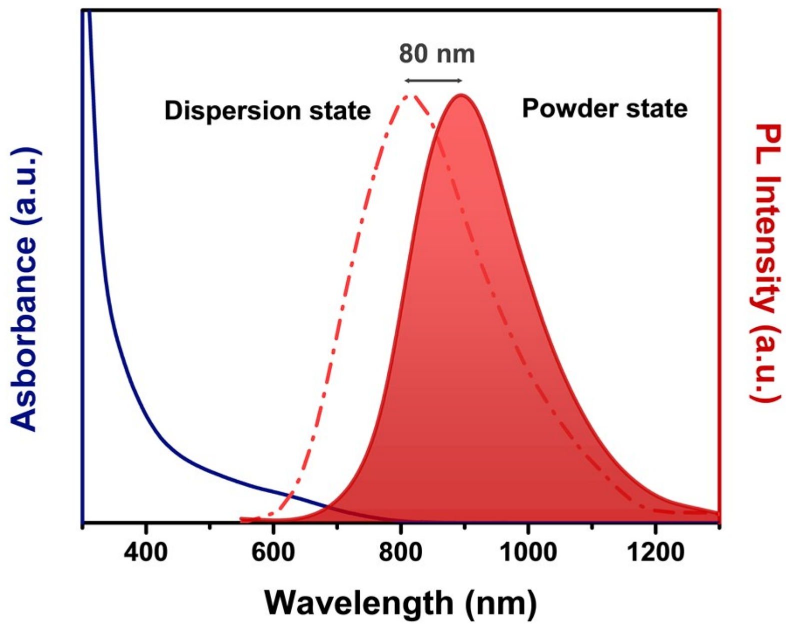

Fig. S6 Red-shift PL of $CuInS_2$/ZnS QDs from dispersion state to powder state in the same absorbance.

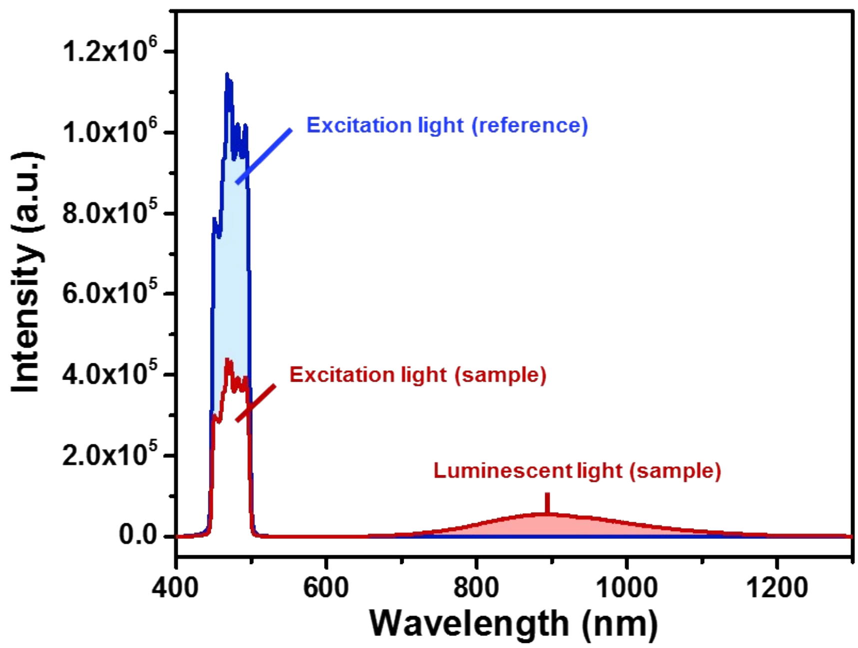

Fig. S7 Excitation light on reference and $CuInS_2$/ZnS QDs photoluminescence spectrum for photoluminescence quantum yield measurement.

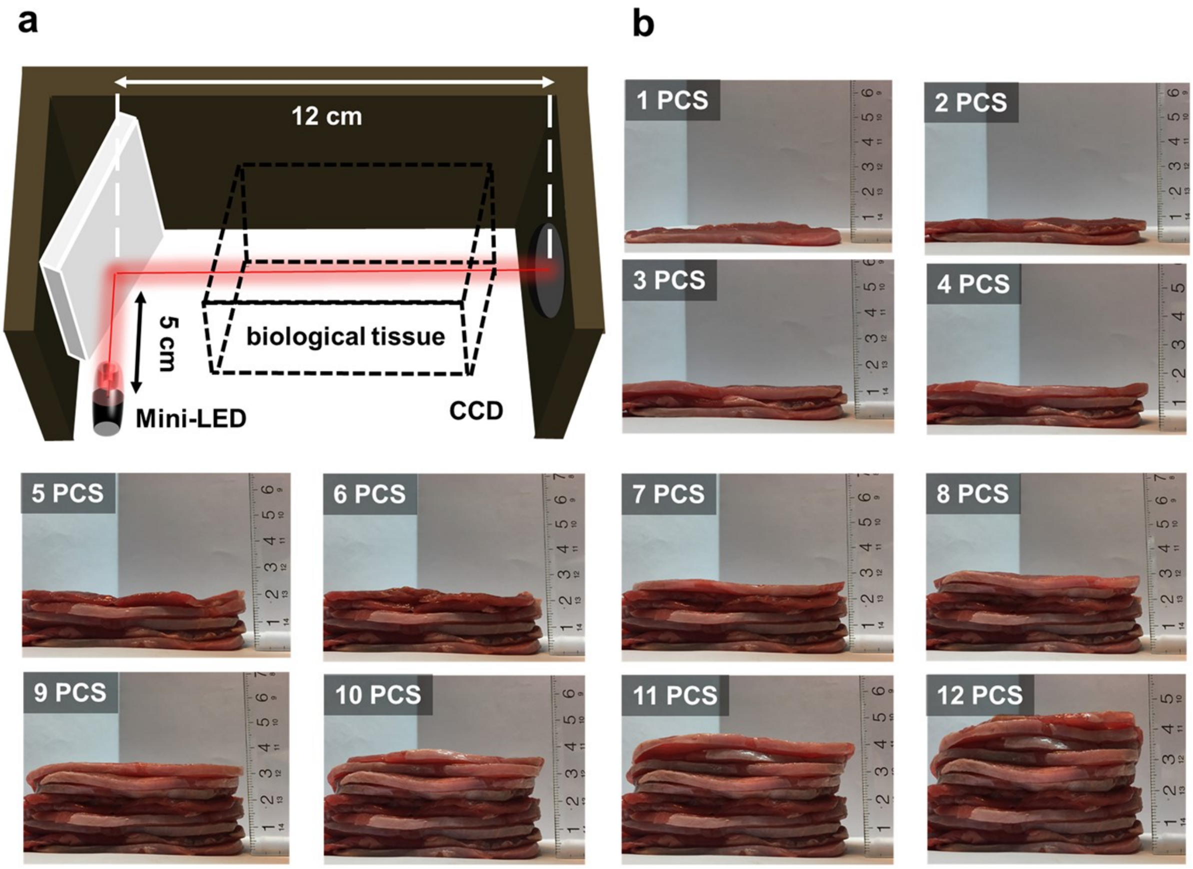

Fig. S8 Detailed experimental design. (a) Schematic diagram of the penetration test and (b) the different thickness of beef slices.