

## Supplementary Information for

### Highly efficient NIR-II luminescent I-III-VI semiconductor

### nanoprobes based on AgInTe<sub>2</sub>:Zn/ZnS nanocrystals

**Authors:** Jiayao Li,<sup>a,b</sup> Tianyong Guan,<sup>a,b</sup> Datao Tu,<sup>\*a,b,c</sup> Wei Lian,<sup>b</sup> Peng Zhang,<sup>b</sup> Siyuan Han,<sup>b</sup> Fei Wen,<sup>b</sup> and Xueyuan Chen<sup>\*a,b,c</sup>

#### **Affiliations:**

<sup>a</sup> College of Chemical Engineering, Fuzhou University, Fujian 350116, China.

<sup>b</sup> CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Key Laboratory of Nanomaterials, and State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.

<sup>c</sup> Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, China.

E-mail addresses: dttu@fjirsm.ac.cn (D. Tu), xchen@fjirsm.ac.cn (X. Chen).

## Experimental Procedures

**Chemicals and materials:** Silver acetate (AgAc), Acetylacetonate Indium ( $\text{In}(\text{acac})_3$ ), and Tri-N-Octylphosphine (TOP) were purchased from Sigma-Aldrich (China). 1-dodecanethiol (DDT) and Tellurium powder (Te) were purchased from Adamas-beta (Shanghai, China). Zinc acetylacetonate ( $\text{Zn}(\text{acac})_2$ ) was purchased from Aladdin (Shanghai, China). 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N- [carboxy-(polyethyleneglycol)-2000] (DSPE-PEG-COOH) were purchased from Shanghai Yare Biotech Inc. Cyclohexane, chloroform, Hydrogen peroxide, ethanol, and Sulfur were purchased from Sinopharm Chemical Reagent Co, China. All chemical reagents were of analytical grade and used as received without further purification unless otherwise noted. Ultrapure water was obtained from Millipore water purification system.

**Characterization:** Powder X-ray diffraction (XRD) patterns of the samples were collected with an X-ray diffractometer (MiniFlex 600, Rigaku) with  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 0.154187$  nm). Both the low- and high-resolution transmission electron microscopy (TEM) measurements were performed by using a TECNAI G<sup>2</sup> F20 TEM equipped with the energy dispersive X-ray (EDX) spectrum. Zeta potential and hydrodynamic diameter distribution of the samples were determined by means of dynamic light scattering (DLS) measurement (Nano ZS ZEN3600, Malvern). X-ray photoemission spectroscopy (XPS) spectra were measured on a SPECS Sage HR 100 spectrometer (thermo fisher ESCALAB250xi) using a non-monochromatised  $\text{Mg-K}\alpha$  radiation of 1253.6 eV and 250 W (monochromatised  $\text{Al-K}\alpha$  radiation of 1486.6 eV and 300 W), in an ultrahigh vacuum chamber at a pressure of  $1 \times 10^{-9}$  mbar. Optical absorption spectra were collected with a Perkin-Elmer Lambda365 UV/Vis spectrometer in transmission mode. Photoluminescence (PL) excitation and emission spectra and PL decays were recorded on the FLS980 spectrometer (Edinburgh) equipped with both continuous xenon (450 W) and pulsed flash lamps. All the spectral data were corrected for the spectral response of both the spectrometer and the integrating sphere.

**PL quantum yield (QY) measurement:** A barium sulfate-coated integrating sphere (150 mm in diameter, Edinburgh) was employed as the sample chamber that was mounted by a fiber optic spectrometer (QE65pro, Ocean Optics) with the entry and output port of the sphere located in  $90^\circ$  geometry from each other in the plane of the spectrometer. The NIR emission in the spectral range of 900-1300 nm for QDs was integrated for the QY determination. All the spectral data collected were corrected for the spectral response of both the spectrometer and the integrating sphere. We calculated the absolute PLQY based on the following equation:

$$PLQY = \frac{N_e}{N_a} = \frac{L_S}{E_r - E_S}$$

where  $N_e$  and  $N_a$  are the photons emitted and absorbed, respectively;  $L_S$  is the

emission intensity,  $E_r$  and  $E_s$  are the intensities of the excitation light in the presence of the pure solution (reference) and  $\text{AgInTe}_2$  (sample) QDs, respectively. All the PLQYs for each sample were measured independently at least three times under identical conditions to yield the average value.

**Stock solution of TOP-Te and TOP-S precursor:** 3 mmol Te and 2.5 mL TOP were added in a 50 mL silica flask containing 7.5 mL of DDT. The mixture was heated to 140 °C and maintained for 10 min until the Te fully dissolved to obtain the stock solution of TOP-Te (0.3 M). 1 mmol Sulfur was dissolved in 10 mL TOP under ultrasonic processing to obtain the stock solution of TOP-S (0.1 M).

**Synthesis of  $\text{Ag}_2\text{Te}$  quantum dots (QDs):** 0.15 mmol AgAc and 0.1 mL TOP were added into a 50 mL silica flask containing 10 mL of DDT. The mixture was heated to 120 °C with vigorously stirring under  $\text{N}_2$  flow and maintained for 5 min to get a clear solution. Subsequently, 1 mL TOP-Te precursor solution was swiftly injected into the reaction mixture under vigorous stirring for 2 min. Finally, the mixture was cooled to RT and washed three times with ethanol and dispersed in 4 mL of cyclohexane or chloroform for further usage.

**Synthesis of  $\text{AgInTe}_2\text{:Zn}$  QDs:**  $\text{AgInTe}_2\text{:Zn}$  QDs were synthesis from  $\text{Ag}_2\text{Te}$  QDs via a cation exchange method. 0.15 mmol AgAc and 0.1 mL TOP were added into a 50 mL silica flask containing 10 mL of DDT. The mixture was heated to 120 °C with vigorously stirring under  $\text{N}_2$  flow and maintained for 5 min to get a clear solution. Subsequently, 1 mL TOP-Te precursor solution was swiftly injected into the reaction mixture under vigorous stirring for 2 min. Then, 0.2 mmol  $\text{In}(\text{acac})_3$  and 0.1 mmol  $\text{Zn}(\text{acac})_2$  were added to the mixture, which was heated to 180 °C and remained at this temperature for 5 min for cation exchange. The mixture was cooled to RT and washed three times with ethanol and dispersed in 4 mL of cyclohexane or chloroform for further usage.

**Synthesis of  $\text{AgInTe}_2\text{:Zn/ZnS}$  QDs:** 0.15 mmol AgAc and 0.1 mL TOP were added into a 50 mL silica flask containing 10 mL of DDT. The mixture was heated to 120 °C with vigorously stirring under  $\text{N}_2$  flow and maintained for 5 min to get a clear solution. Subsequently, 1 mL TOP-Te precursor solution was swiftly injected into the reaction mixture under vigorous stirring for 2 min. Then, 0.2 mmol  $\text{In}(\text{acac})_3$  and 0.1 mmol  $\text{Zn}(\text{acac})_2$  were added to the mixture, which was heated to 180 °C and remained at this temperature for 5 min for cation exchange. After that, the mixture was heated to 220 °C. 0.2 mL TOP-S precursor solution was slowly added into the reaction solution in 20 min for ZnS coating. The mixture was cooled to RT and washed three times with ethanol and dispersed in 4 mL of cyclohexane or chloroform for further usage.

**Etching of  $\text{AgInTe}_2\text{:Zn}$  QDs:** 0.5 mL OA and 0.5 mmol benzoyl peroxide were added in 2 mL chloroform to get the BPO solution, which was added in 1 mL of the

as-prepared AgInTe<sub>2</sub>:Zn QDs solution. After 30 min etching, the mixture was cooled to RT and washed three times with ethanol and dispersed in 4 mL of cyclohexane or chloroform for further usage.

***Synthesis of Lipo coated AgInTe<sub>2</sub>:Zn/ZnS QDs (Lipo-QDs):*** In a typical process, 10 mg of the as-synthesized AgInTe<sub>2</sub>:Zn/ZnS QDs were dispersed in 10 mL chloroform solution containing 40 mg of DSPE-PEG-COOH in a 25 mL round-bottom flask, which was sonicated for 5 min. The mixture was then dried in a rotary evaporator under reduced pressure at 40 °C to form a lipid film on the inside wall of the flask. The lipid film was hydrated with 4000 mL ultrapure water. The QDs became soluble after vigorous sonication for 5 min. The excess lipids were removed from the Lipo-coated QDs by centrifugation at 21000 rpm for 20 min. The resulting Lipo-QDs were washed with ultrapure water and finally redispersed in ultrapure water for the following use.

***H<sub>2</sub>O<sub>2</sub> detection based on Lipo-QDs:*** Typically, 100 µL of Lipo-QDs was mixed with 100 µL of deionized water containing different amounts (0-50 nM) of H<sub>2</sub>O<sub>2</sub> in a 96-well microplate. After incubation at 37 °C for 3 h, the microplate was subjected to PL measurement upon 808-nm laser excitation on a fluorescence spectrometer coupled with a multimodal microplate reader. Five independent experiments were carried out to yield the average value and standard deviation.

***Xanthine oxidase (XO) detection based on Lipo-QDs:*** Typically, 50 µL of Lipo-QDs was mixed with 50 µL 1µM xanthine (XA) solution and 100 µL of Tris-HCl buffer solution (10 mM, pH 7.4) containing different amounts (0.05-5000 µU) XO in a 96-well microplate. After incubation at 37 °C for 3 h, the microplate was subjected to PL measurement upon 808-nm laser excitation on a fluorescence spectrometer coupled with a multimodal microplate reader. Five independent experiments were carried out to yield the average value and standard deviation.

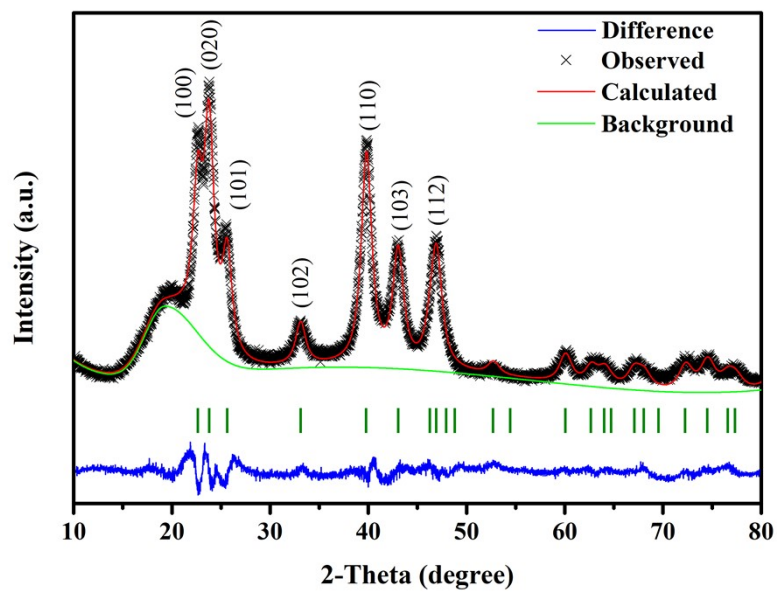
**Table S1.** Rietveld refinement of  $\text{AgInTe}_2$  and  $\text{AgInTe}_2:\text{Zn}$ .  $R_p$ : Profile residual.  $R_{wp}$ : Weighted profile residual.  $\text{CHI}^2$ :  $(R_{wp}/R_{exp})^2$ .  $R_{exp}$ : Expected profile residual. The doping of  $\text{Zn}^{2+}$  (5.4 mol%) in  $\text{AgInTe}_2$  may result in the expansion of unit cell, which was ascribed to the doping of  $\text{Zn}^{2+}$  in the interstitial positions of the lattice

Samples	Lattice parameter		Residuals		
	a = b (Å)	c (Å)	$R_{wp}$ (%)	$R_p$ (%)	$\text{CHI}^2$ (%)
<b><math>\text{AgInTe}_2</math></b>	<b>4.5243</b>	<b>7.4635</b>	<b>7.54%</b>	<b>5.63%</b>	<b>2.02</b>
<b><math>\text{AgInTe}_2:\text{Zn}</math></b>	<b>4.5315</b>	<b>7.4715</b>	<b>9.34%</b>	<b>6.89%</b>	<b>2.82</b>

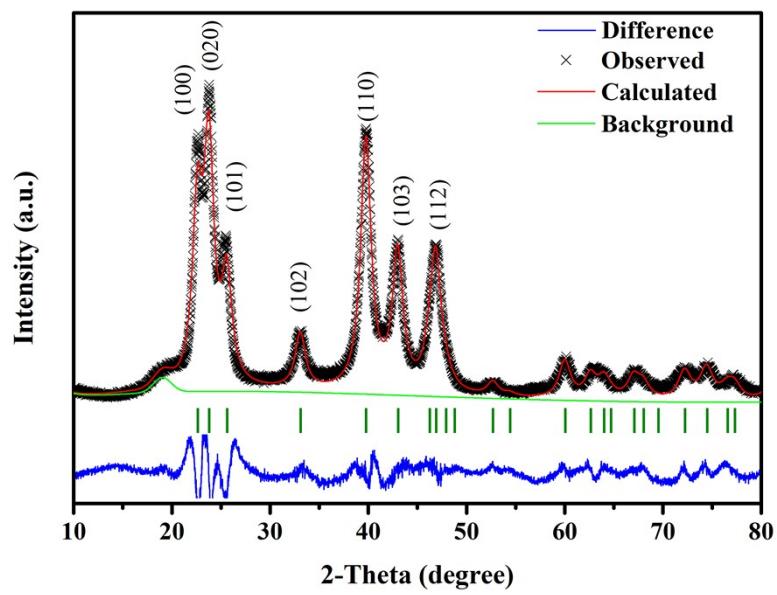
**Table S2.** PL lifetimes of AgInTe<sub>2</sub>, AgInTe<sub>2</sub>:Zn, and AgInTe<sub>2</sub>:Zn/ZnS QDs, respectively. The PL decays of these QDs were fitted by bi-exponential function:

$$I(t) = a_1 \exp(-t/t_1) + a_2 \exp(-t/t_2) + I_0$$

Samples	A <sub>1</sub>	τ <sub>1</sub> (ns)	A <sub>2</sub>	τ <sub>2</sub> (ns)
AgInTe <sub>2</sub>	0.334	12.8	0.527	99.4
AgInTe <sub>2</sub> :Zn	0.321	25.5	0.553	198.4
AgInTe <sub>2</sub> :Zn/ZnS	0.498	159.5	0.436	575.4

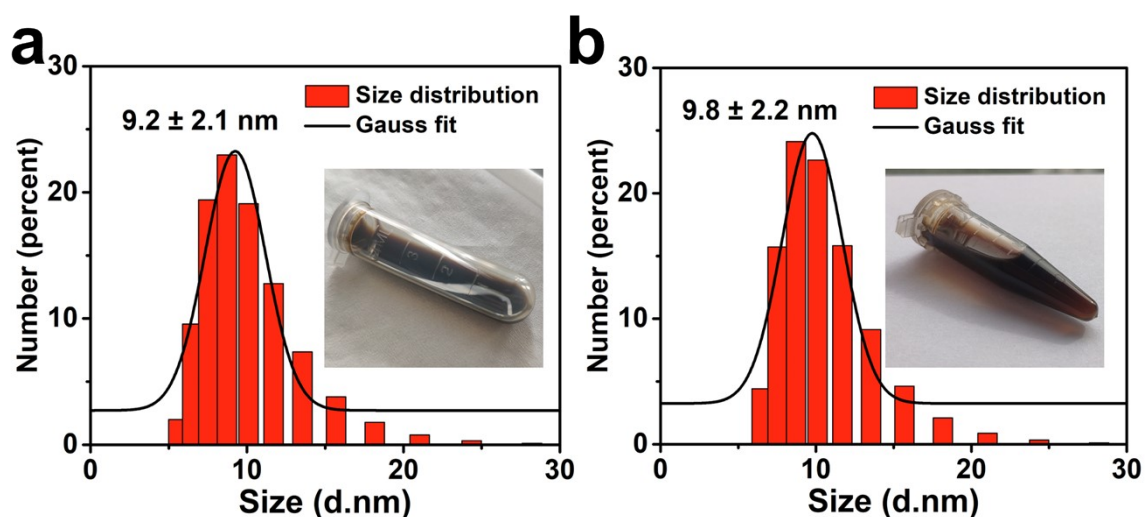


**Fig. S1.** Rietveld refinement of XRD patterns for AgInTe<sub>2</sub>.

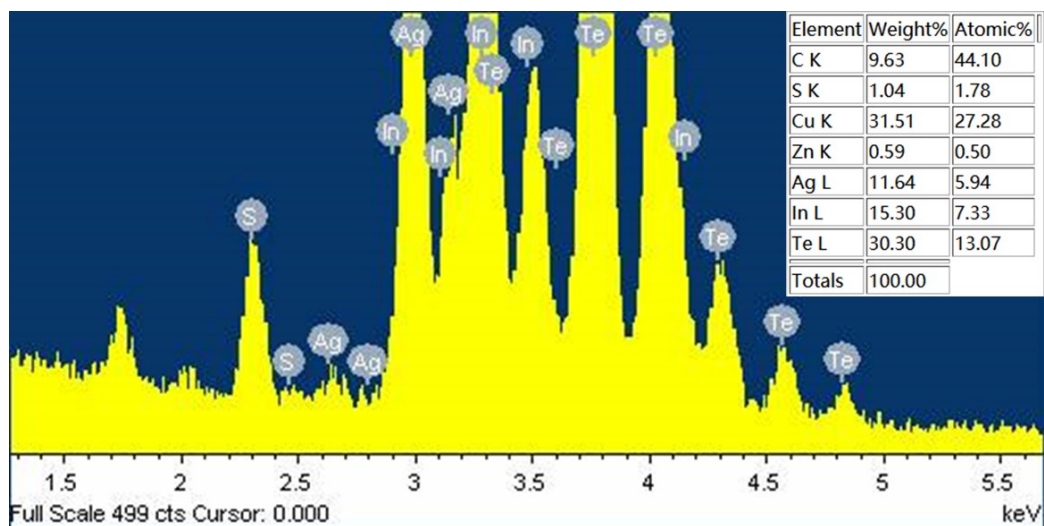


**Fig. S2.** Rietveld refinement of XRD patterns for AgInTe<sub>2</sub>:Zn.

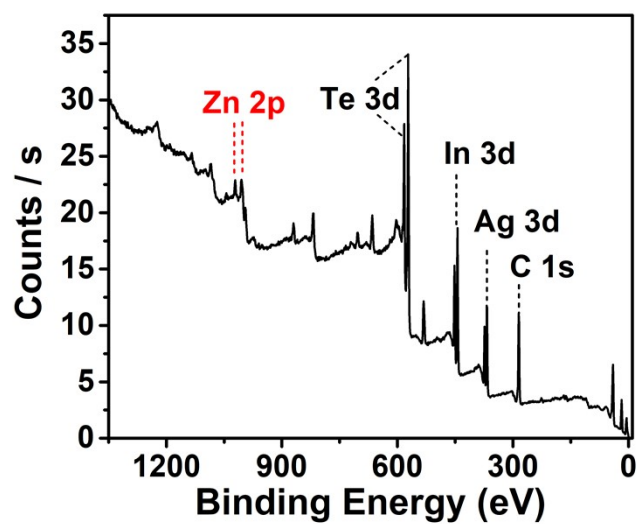




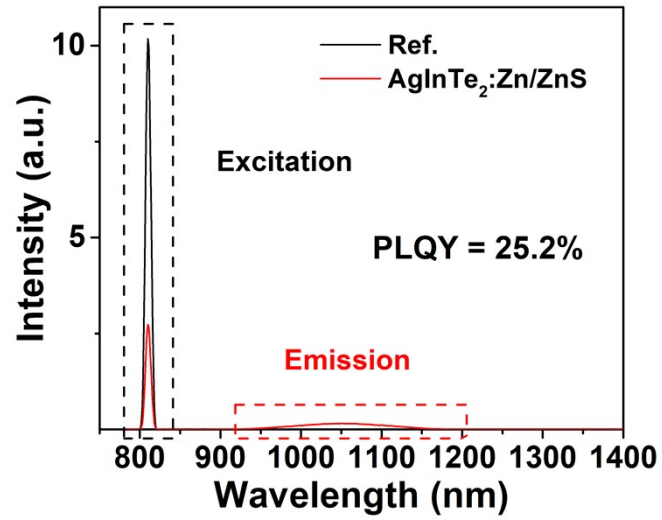
**Fig. S3.** Size distribution and corresponding photo (inset) of AgInTe<sub>2</sub>:Zn/ZnS QDs in cyclohexane (a) before and (b) after 12000 rpm centrifugation. It can be observed that no aggregations with large sizes formed in the solvents. Moreover, the size distribution remained essentially unaltered even after 12000 rpm centrifugation, which confirms the excellent colloidal stability of AgInTe<sub>2</sub>:Zn/ZnS QDs.



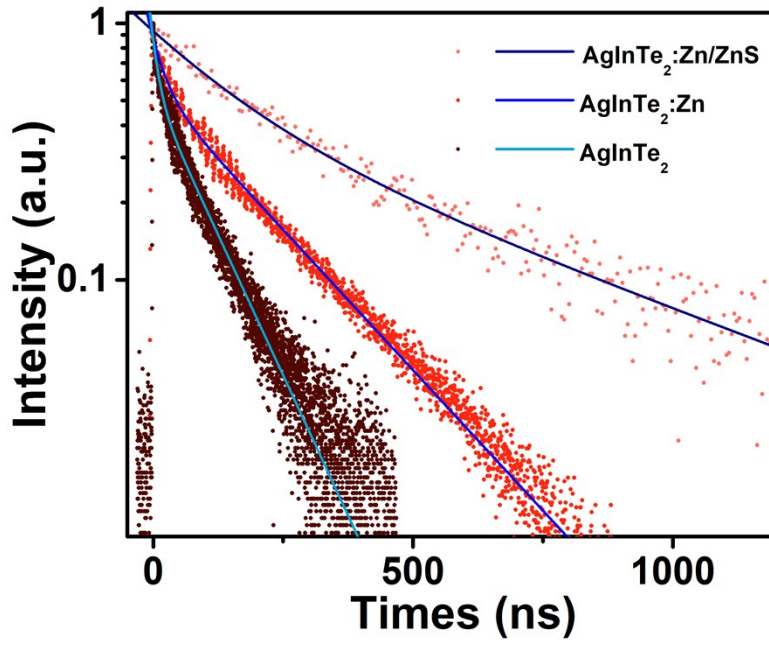
**Fig. S4.** EDX spectrum of the synthesized  $\text{AgInTe}_2\text{:Zn/ZnS}$  QDs. It reveals the existence of Ag, In, Te, Zn, S elements in the QDs.



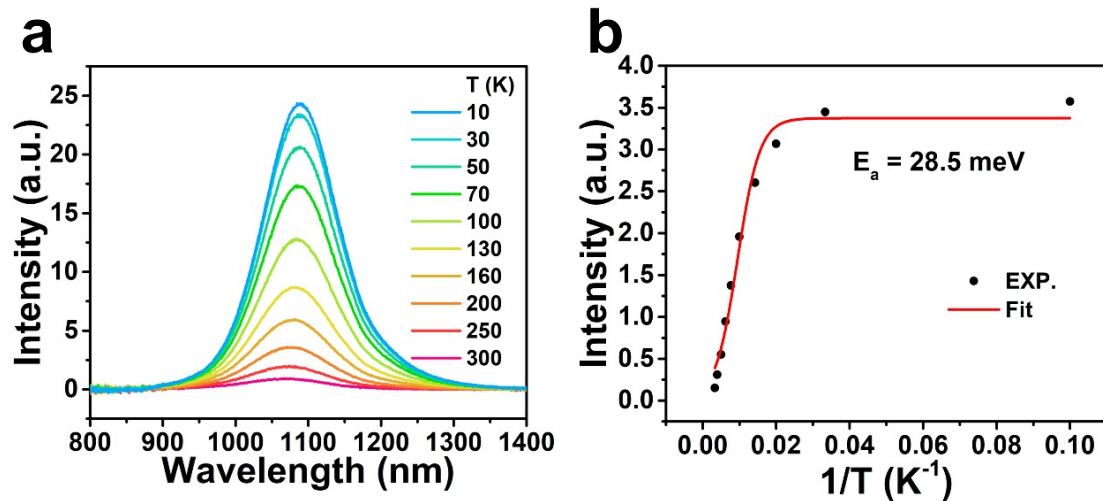
**Fig. S5.** XPS analysis of AgInTe<sub>2</sub>:Zn/ZnS QDs. The spectra were corrected by C-C bond at 284.8 eV. The Zn 2p peak shows a relatively low zinc concentration in QDs, which is in consistent with the result of EDX spectrum.



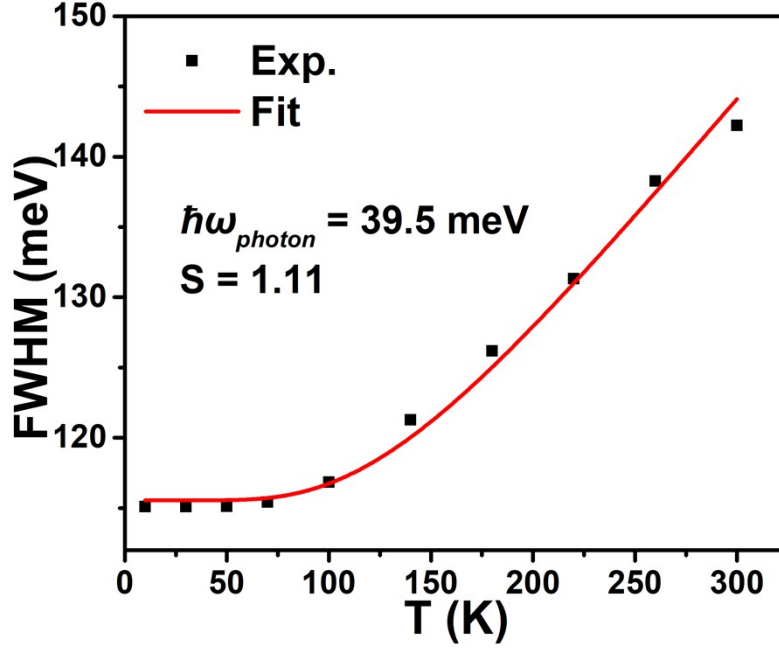
**Fig. S6.** Absolute PLQY measurement of the AgInTe<sub>2</sub>:Zn/ZnS QDs excited at 808 nm. The integrated intensity of emission (marked with red dash) and excitation (marked with black dash) were used for absolute PLQY calculation.



**Fig. S7.** PL decays (dots) and fitting curves (solid lines) of  $\text{AgInTe}_2$ ,  $\text{AgInTe}_2:\text{Zn}$ , and  $\text{AgInTe}_2:\text{Zn}/\text{ZnS}$  QDs, respectively. The PL decays of these QDs were fitted by bi-exponential function:  $I(t) = a_1 \exp(-t/t_1) + a_2 \exp(-t/t_2) + I_0$ .



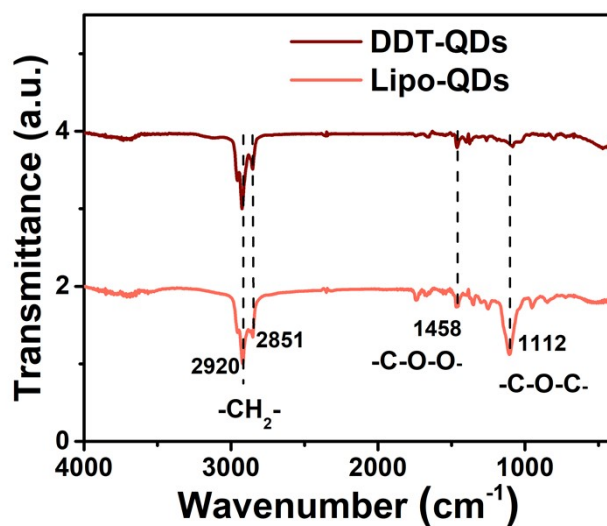
**Fig. S8.** (a) Temperature-dependent PL emission spectra. (b) Thermal activation energy ( $E_a$ ) fitting of AgInTe<sub>2</sub>:Zn QDs. It can be observed that the PL intensity decreased with increasing the temperature from 10 to 300 K. According to the fitting result, the  $E_a$  of the as-synthesized AgInTe<sub>2</sub>:Zn QDs was determined to be 28.5 meV.



**Fig. S9.** Full width at half maxima (FWHM) of AgInTe<sub>2</sub>:Zn/ZnS QDs as a function of temperature. We calculated the Huang-Rhys factor of AgInTe<sub>2</sub>:Zn/ZnS QDs from the temperature-dependent PL spectra using the following equation:

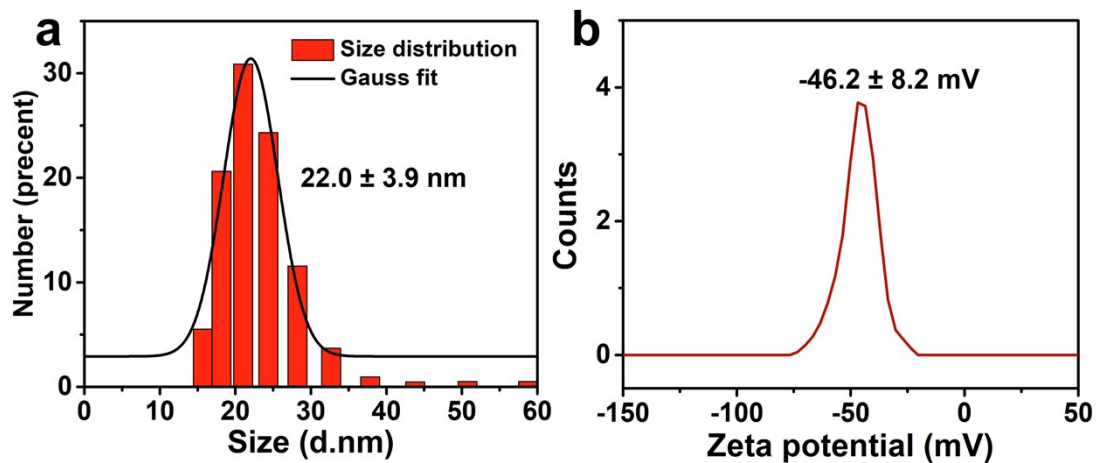
$$FWHM = 2.36\sqrt{S}\hbar\omega_{phonon} \sqrt{\coth \frac{\hbar\omega_{phonon}}{2k_bT}}$$

The phonon energy ( $\hbar\omega_{phonon}$ ) and the Huang-Rhys factor (S) were calculated to be 39.5 meV and 1.11. Such a low value of Huang-Rhys factor indicates a weak electron-phonon coupling that explains the small Stokes shift of the AgInTe<sub>2</sub>:Zn/ZnS QDs.

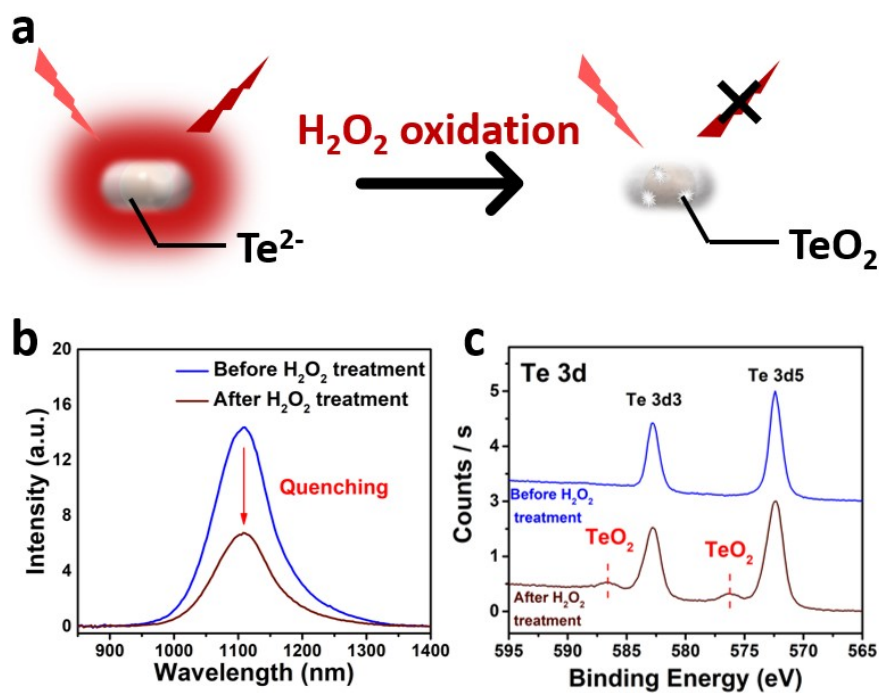


**Fig. S10.** FTIR spectra of the  $\text{AgInTe}_2\text{:Zn/ZnS}$  QDs with different surface ligands. For the as-synthesized  $\text{AgInTe}_2\text{:Zn/ZnS}$  QDs, the asymmetric and symmetric stretching vibrations of methylene ( $-\text{CH}_2-$ ) in the long alkyl chain of DDT peaking at 2920 and 2851  $\text{cm}^{-1}$ . After modification with Lipo, a new peak at 1112  $\text{cm}^{-1}$  appeared, which can be ascribed to the stretching vibrations of the C–O–C bond in phospholipid, indicating that the Lipo phospholipid was successfully assembled on the surface of  $\text{AgInTe}_2\text{:Zn/ZnS}$  QDs.

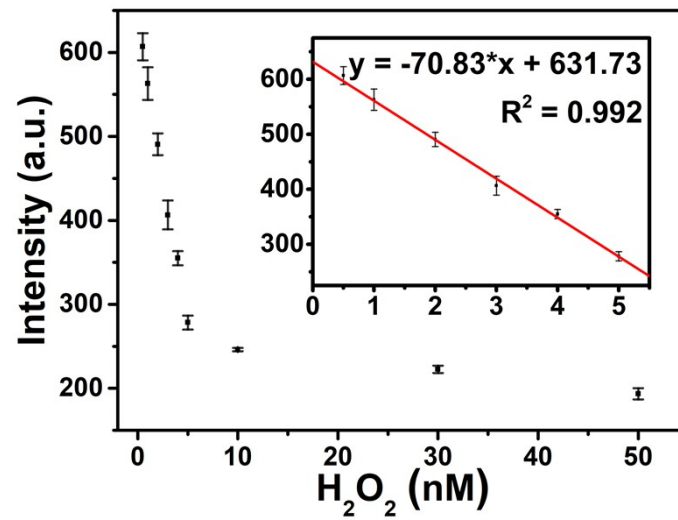




**Fig. S11.** (a) Size distribution and (b) Zeta-potential of Lipo-AgInTe<sub>2</sub>:Zn/ZnS QDs dispersed in aqueous solution (pH 7). The Lipo-QDs had a mean size of 22.0 nm, which is larger than that of DDT-QDs (16.9 nm) due to the DSPE-PEG assembled on the surface. The  $\zeta$  potential for Lipo-QDs was determined to be  $-46.2 \pm 8.2$  mV due to the oxhydryl groups on the surface of the QDs.



**Fig. S12.** (a) Scheme for the homogeneous assay of  $\text{H}_2\text{O}_2$  based on  $\text{AgInTe}_2\text{:Zn/ZnS}$  nanoprobes. (b) PL intensity and (c) XPS of  $\text{AgInTe}_2\text{:Zn/ZnS}$  QDs before and after  $\text{H}_2\text{O}_2$  treatment. The  $\text{AgInTe}_2\text{:Zn/ZnS}$  QDs exhibited the characteristic peaks of Te 3d5 and Te 3d3 at 572.4 and 582.8 eV. After  $\text{H}_2\text{O}_2$  treatment, two additional peaks at binding energies of 576.2 and 586.5 eV appeared that can be attributed to the Te-O bonding states. The oxidation of  $\text{AgInTe}_2\text{:Zn/ZnS}$  QDs produced new localized surface defect sites for nonradiative exciton recombination, causing dramatic PL quenching.



**Fig. S13.** Calibration curve for the H<sub>2</sub>O<sub>2</sub> assay based on the AgInTe<sub>2</sub>:Zn/ZnS nanoprobe. Inset shows the linear range (0.5-5 nM) of the calibration curve.