Electronic Supplementary Information

Origin of highly efficient photoluminescence in $AgIn_5S_8$ nanoparticles

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The theoretical estimation processes of QY_{D1} and QY_{D2}

The quantum yields of the surface defects (QY_{D1}) and the intrinsic defects (QY_{D2}) were estimated from the experimentally obtained QYs (Fig. 6b) and the diameters (Fig. S7). In other words, QY of the defect emission was expressed by QY_{D1} and QY_{D2} under the assumption that QY_{D1} and QY_{D2} were independent of the reaction temperature and the diameter.

$$QY = P_S \times QY_{D1} + P_I \times QY_{D2} \quad \text{(S-1)}$$

where P_S is the relative population of the surface defects and P_I is the relative population of the intrinsic defects as a function of the reaction temperature. Under the assumption that the surface defects and intrinsic defects were related to the surface area and the volume, respectively, P_S and P_I were estimated from the surface-to-volume ratio of the nanoparticles. In addition, the decreasing densities of the surface and intrinsic defects with increasing reaction temperature were taken into account, because the normalized intensities of defect emission (D1′ and D2′) decreased with increasing temperature (Fig. 6a). In other words, the emission intensity of the surface and intrinsic defects in the given surface area and the volume, respectively, decreased with the reaction temperature, which was attributed to the reduced defect density at high temperatures.

Accordingly, from the surface-to-volume ratio and the reaction temperature dependence, the values of P_S and P_I were simulated, which were employed to calculate QY_{D1} and QY_{D2}. Indeed, the values of QY_{D1} and QY_{D2} were estimated from four equations, where each equation was based on the nanoparticles synthesized at 120, 140, 160, and 180 °C with different values of P_S and P_I (Eq. S-1). As a result, the most reasonable values of QY_{D1} and QY_{D2} were calculated to be 0.40 and 0.23, respectively. To validate the calculation results, the relative intensities of the defect emission (I_{D1}/I_{D2}) were obtained from the calculated values of QY_{D1}, QY_{D2}, P_S, and P_I, which agreed well with the experimental results (Fig. 6b) and confirmed the validity of the theoretical estimation processes for QY_{D1} and QY_{D2}.

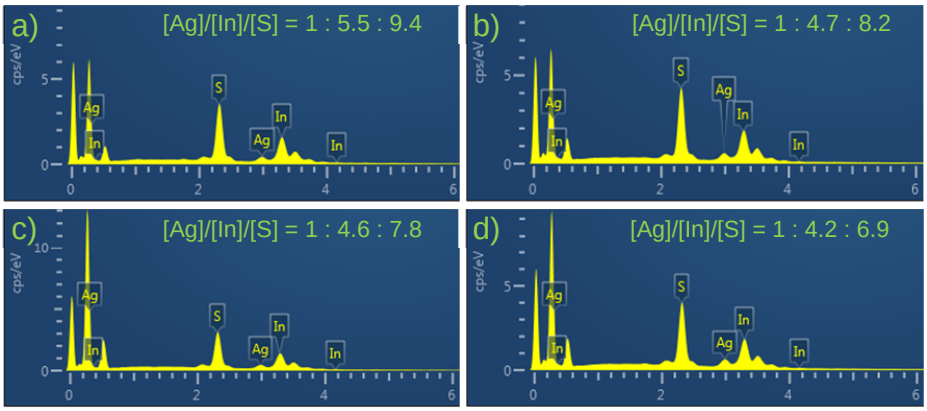

Figure S1. EDS analyses of the nanoparticles synthesized at (a) 120 °C, (b) 140 °C, (c) 160 °C and (d) 180 °C show the chemical formula of $AgIn_5S_8$.

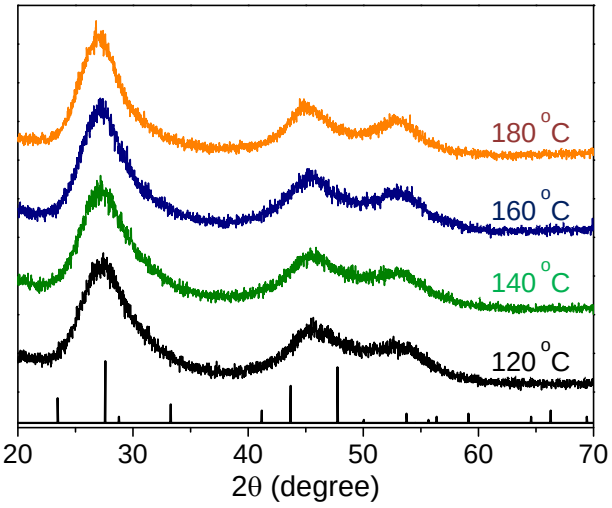

Figure S2. XRD patterns of the $AgIn_5S_8$ nanoparticles synthesized at 120 °C, 140 °C, 160 °C and 180 °C are compared to that of the cubic phase (JCPDS 00-026-1477).

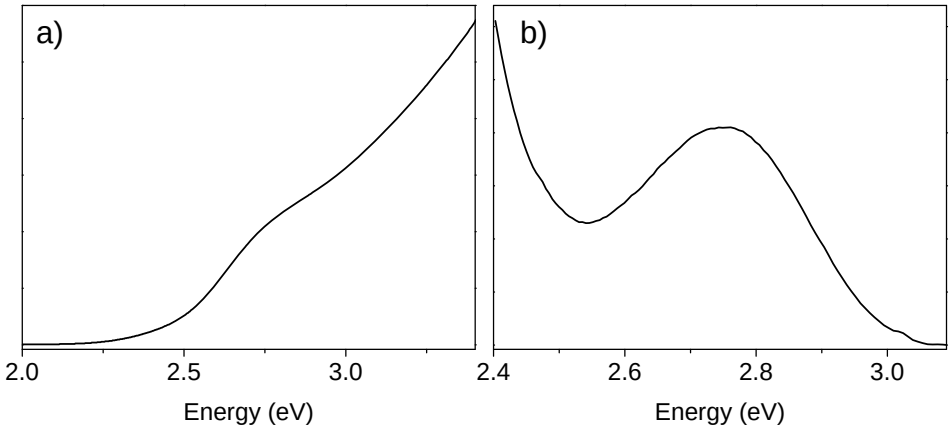

Figure S3. (a) The absorption spectrum and (b) the PL spectrum of the $AgIn_5S_8$ nanoparticles in the band gap region.

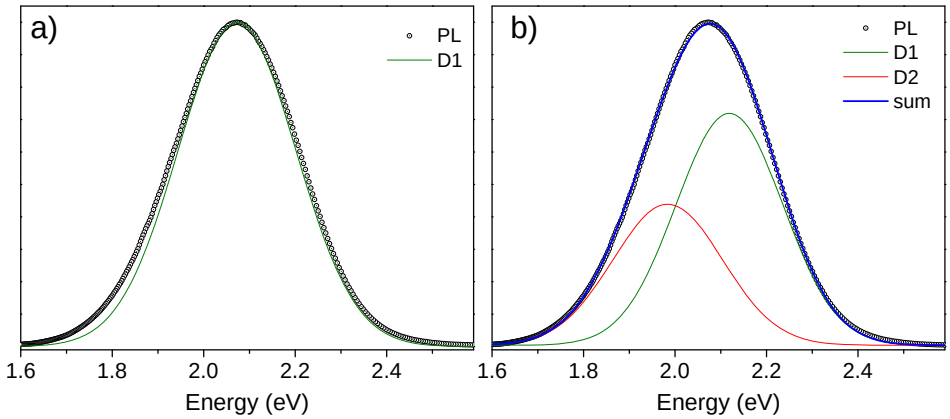

Figure S4. The defect emission is decomposed by (a) single Gaussian function and (b) two Gaussian functions.

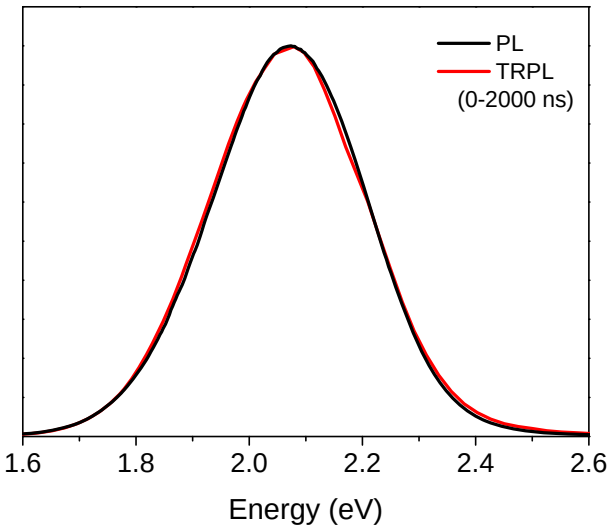

Figure S5. The steady-state PL spectrum is almost identical to the TRPL spectrum integrated for the temporal range of 0-2000 ns.

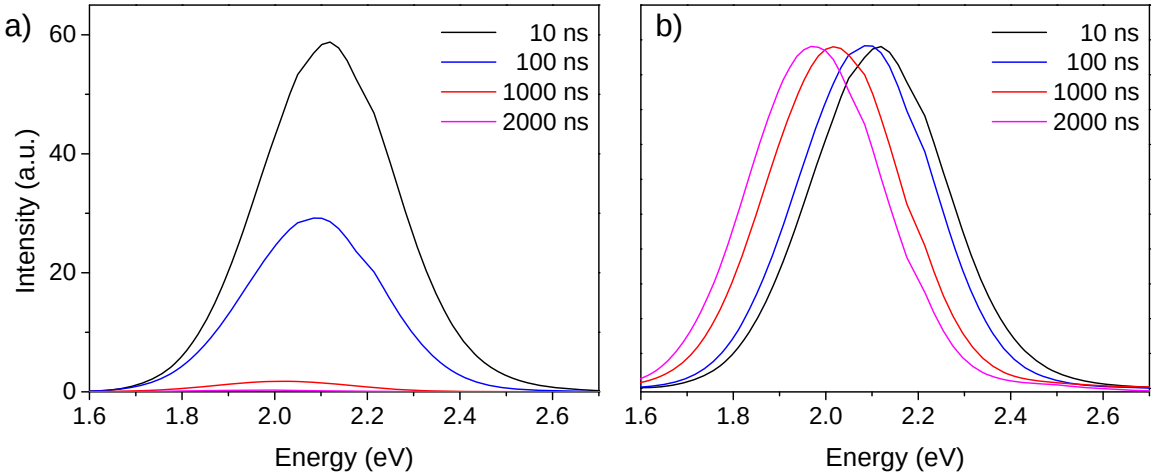

Figure S6. The TRPL spectra of the $AgIn_5S_8$ nanoparticles show (a) the decrease in emission intensity and (b) the red-shifted peak energy, which is normalized for better comparison.

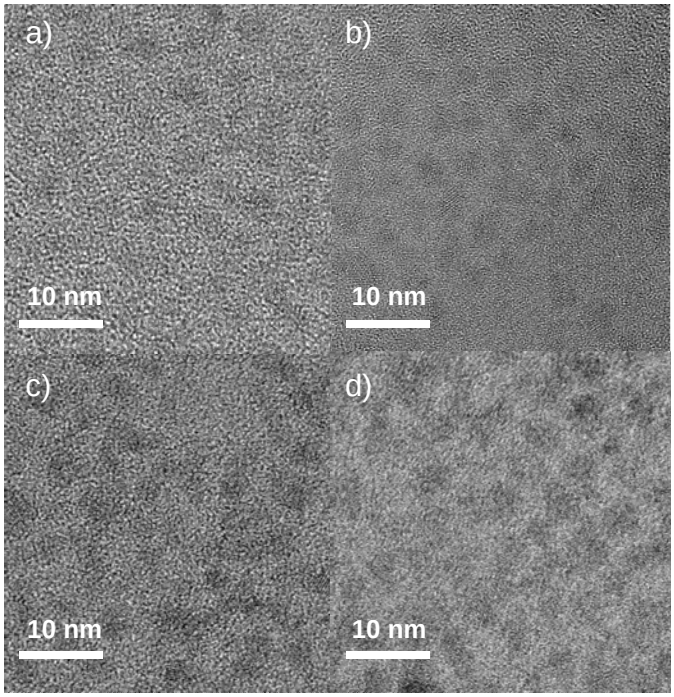

Figure S7. TEM images of the $AgIn_5S_8$ nanoparticles synthesized at (a) 120 °C, (b) 140 °C, (c) 160 °C, and (d) 180 °C.

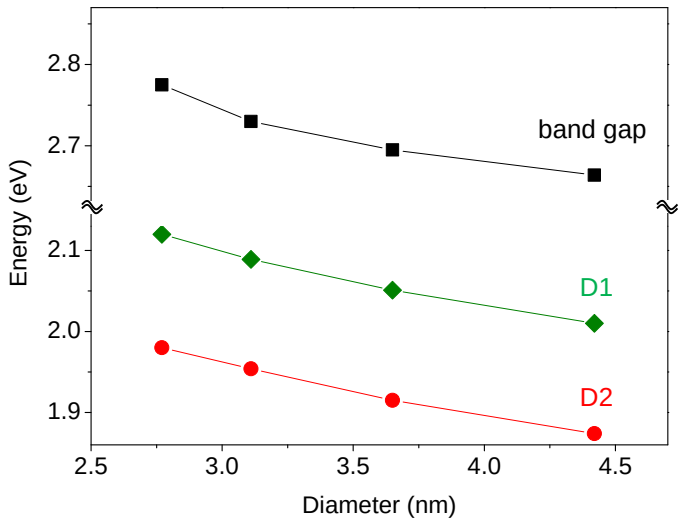

Figure S8. The band gap (black), surface defect emission (D1, green), and intrinsic defect emission (D2, red) energies are plotted as a function of the nanoparticle size.

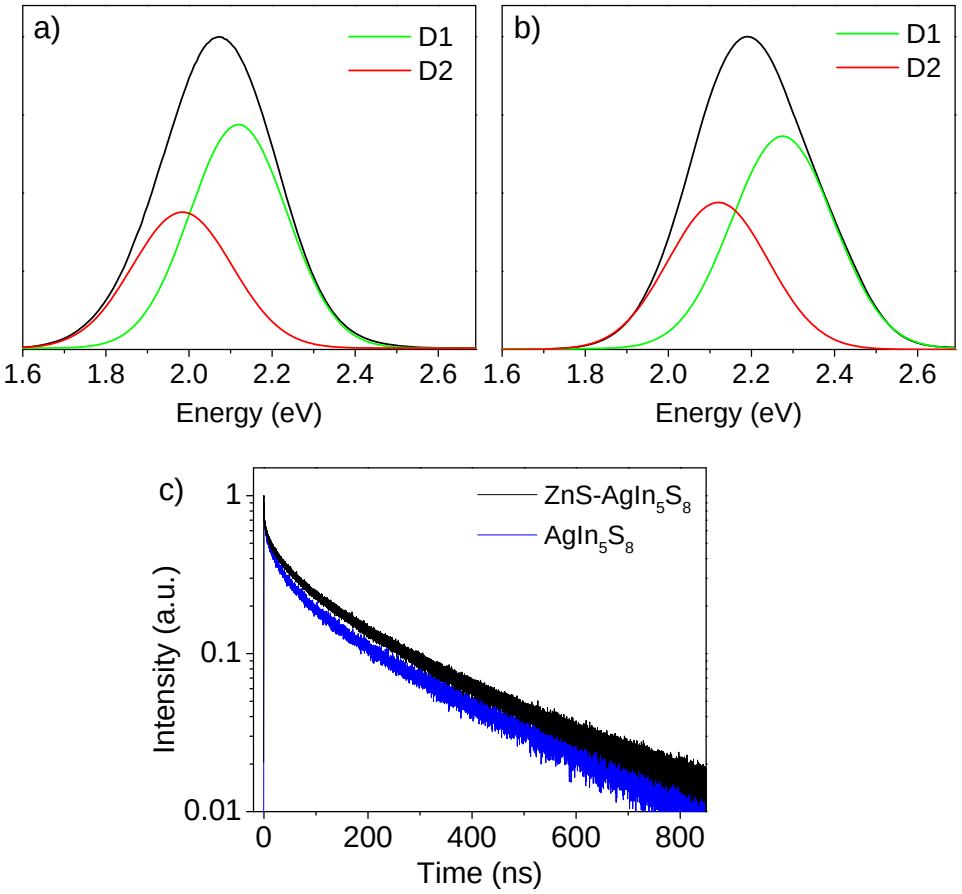

Figure S9. The PL spectra of (a) $AgIn_5S_8$ nanoparticles and (b) ZnS-$AgIn_5S_8$ nanoparticles show the change of the relative contribution between D1 and D2. (c) The decay profiles of defect emission of $AgIn_5S_8$ and ZnS-$AgIn_5S_8$ nanoparticles.