Electronic Supplementary Information for

Crystal Phase-Controlled Synthesis of Rod-Shaped $AgInTe_2$ Nanocrystals for *in vivo* Imaging in the Near-Infrared Wavelength Region

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Experimental Section

1. Characterization of $AgInTe_2$ nanocrystals (NCs)

1.1 Materials

Indium(III) acetate, tellurium, and indocyanine green were purchased from Sigma Aldrich. Zinc(II) acetate, 1-dodecanethiol (DDT), trioctylphosphine (TOP), and octane were obtained from Wako Chemicals. Other chemicals were supplied by Kishida Reagents Chemicals.

1.2 Characterizations of $AgInTe_2$ NCs

The chemical compositions of the $AgInTe_2$ NCs were determined by energy-dispersive X-ray analysis (Horiba, EMAX Energy EX-250) or X-ray fluorescence spectroscopy (Rigaku, EDXL-300). The sizes and shapes of the NCs were observed by transmission electron microscopy (TEM; Hitachi H-7650) at an operating voltage of 100 kV. The size distributions were obtained by measuring the dimensions of particles observed in the TEM images (more than 100 particles). The crystal structures were determined by powder X-ray diffraction (XRD) analysis using a Rigaku Smart-Lab with CuKα radiation. UV-visible-near-infrared absorption spectra were obtained with a JASCO V-670 spectrophotometer, and PL spectra were acquired with a Horiba Nanolog fluorescence spectrophotometer. Photoluminescence quantum yield (QY) was determined using indocyanine green as a standard reference (QY = 13.2% in ethanol)[1] for near-infrared photoluminescence with excitation at 700 nm. The relative PL QY of $AgInTe_2$ was calculated by using the following equation,

$$QY = QY_R \frac{I \, A_R \, n^2}{I_R \, A \, n_R^2}$$

where QY is the quantum yield of samples, I is the measured integrated PL intensity, n is the refractive index of solvent, and A is the absorbance at the excitation wavelength (typically 0.1). The subscript R refers to the parameters of the standard reference.

1.3 Crystal structure simulation of hexagonal $AgInTe_2$

The authentic diffraction pattern for the hexagonal wurtzite crystal phase of $AgInTe_2$ was not available in the International Center for Diffraction Data (PDF-2) or any literature. Therefore, we simulated the XRD pattern of hexagonal $AgInTe_2$ according to the method previously reported for the simulation of the XRD pattern of wurtzite $CuInS_2$.[2] The crystal structure analysis software Rietan-FP was used for the calculation.[3] The lattice constant was estimated by substituting the d-spacing values of the $AgInTe_2$ NCs determined by XRD measurement for those of the wurtzite crystal structure of ZnS; the *hkl* values of the diffraction peaks in the XRD patterns of the $AgInTe_2$ NCs were obtained by analogy with the patterns of wurtzite ZnS. The detailed information regarding crystal structure data are shown in Tables S1 and S2.

Table S1 Crystal data of $AgInTe_2$ used for XRD pattern simulation

Formula	Crystal system	Space group	Lattice constant / Å	
			a and *b*	*c*
$AgInTe_2$	Hexagonal	$P6_3mc$ (No.186)	4.521	7.449

Table S2 Atomic coordinates of hexagonal $AgInTe_2$ used for XRD pattern simulation

Atom	x/a	y/b	z/c	Occupancy
Te	1/3	2/3	0	1
In	1/3	2/3	0.3752	0.5
Ag	1/3	2/3	0.3752	0.5

2. Incorporation of $AgInTe_2$ NCs into liposomes

2.1 Preparation of liposome-$AgInTe_2$ composites

To demonstrate the performance of $AgInTe_2$ as near-infrared light emitting materials for *in vivo* imaging, it is necessary to disperse the hydrophobic $AgInTe_2$ NCs in a hydrophilic media. Thus, the as-prepared $AgInTe_2$ NCs were encapsulated into small unilamellar liposomes according to a previously reported method for the preparation of liposome-CdSe NC nanocomposites.[4] Furthermore, chloroform solution containing 8.26 nmol(particles) $AgInTe_2$ NCs prepared at 180°C was placed into a test tube. The amount of $AgInTe_2$ NCs was determined from the absorption coefficient of $AgInTe_2$ NCs at 700 nm (1.42×10^6 dm^3 mol^{-1}(particles) cm^{-1}; Fig. S5). A 770-mm^3 portion of chloroform solution containing 8.86 μmol 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) was added to the test tube and vigorously stirred until the solution became clear. Chloroform was then evaporated under reduced pressure to obtain a DSPC-$AgInTe_2$ composite film. The obtained film was hydrated by the addition of 3 cm^3 culture media [Dulbecco's modified Eagle's medium (DMEM)/F12 [11320, Gibco®, Thermo Fisher Scientific, USA] containing 20% fetal bovine serum (FBS: Trace Scientific Ltd., Australia) and 100 U/cm^3 penicillin/streptomycin]. Since the resulting dispersion contained multilamellar liposomes, the ultrasonication of the solution was conducted for 1 min at 65°C followed by centrifugation at 4000 rpm for 1 min to remove large liposomes from the dispersion. The resulting dispersion contained predominantly unilamellar liposomes composed of DSPC-$AgInTe_2$ composites. The average hydrodynamic diameter was determined to be 1.8×10^2 nm by dynamic light scattering (DLS; Otsuka Electronics FDLS-3000H).

3. *In vivo* photoluminescence imaging of mice injected with $AgInTe_2$ NCs

C57BL/6 mice were purchased from SLC Japan. The mice were housed in a controlled environment (12 h light/dark cycles at 21°C) with free access to water and an alfalfa-free diet before sacrifice. All conditions and handing of animals in this study were conducted under protocols approved by the Nagoya University Committee on Animal Use and Care. For *in vivo* PL imaging studies, we used the mice given food containing no fluorescent components for one week to diminish the effect of autogenic fluorescence from mice. The dispersions of DSPC-$AgInTe_2$ composite liposomes were prepared by the dilution of original dispersion with phosphate-buffered saline (pH 7.4). After the injection of 50 mm^3 dispersion of DSPC-$AgInTe_2$ composite liposomes, the mice were anesthetized and then monitored with an SAI-1000 portable *in vivo* fluorescent imaging system (SHIMADZU; excitation filter, 980 nm; emission filter, 900 nm long-pass).

Results

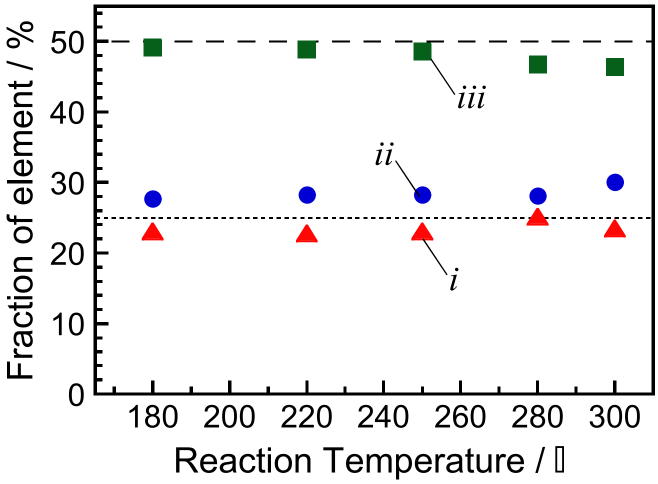

Fig. S1 The fractions of Ag (*i*), In (*ii*), and Te (*iii*) in $AgInTe_2$ NCs prepared at different reaction temperatures. The lines show the stoichiometric fractions of Ag and In (dotted lines) and that of Te (broken line).

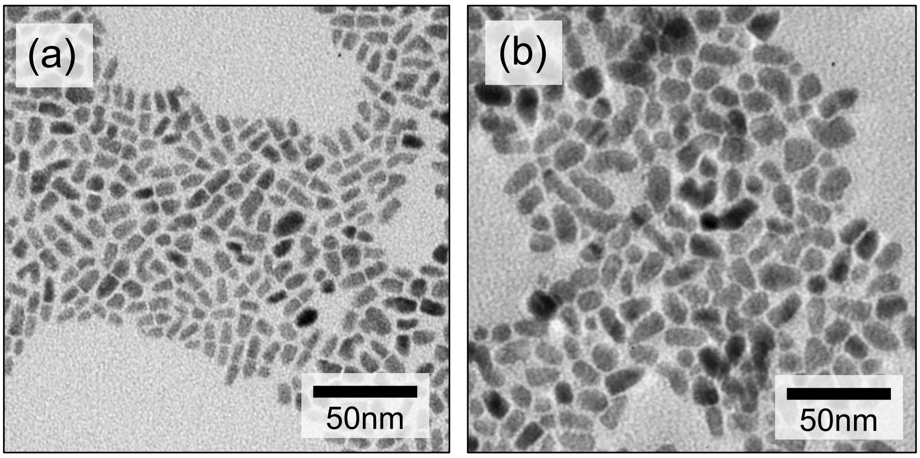

Fig. S2 TEM images of $AgInTe_2$ NCs prepared at (a) 220°C and (b) 280°C.

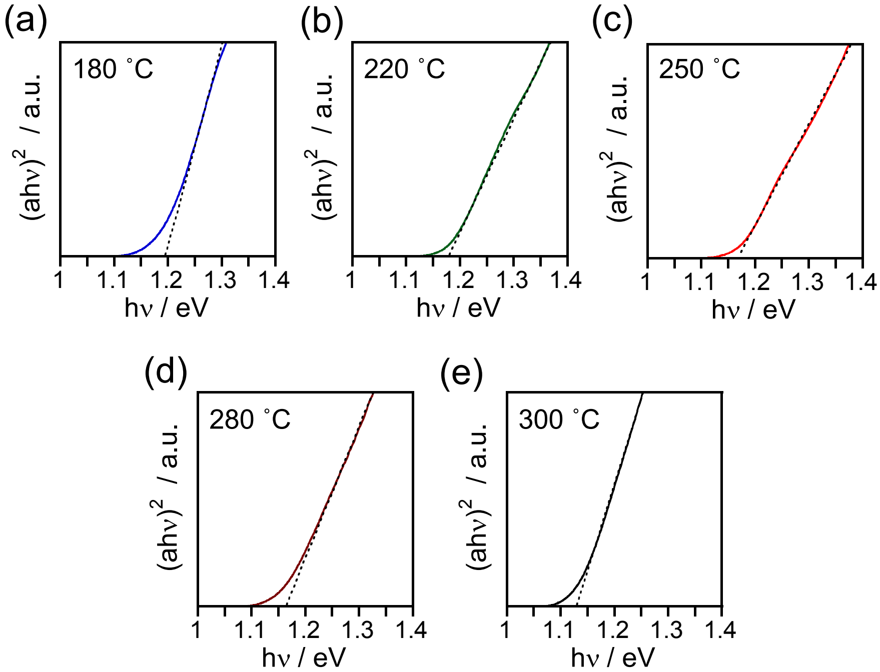

Fig. S3 Tauc plots used to determine the E_g of $AgInTe_2$ NCs. The absorption spectra of nanocrystals prepared at (a) 180°C, (b) 220°C, (c) 250°C, (d) 280°C, and (e) 300°C were used for these plots.

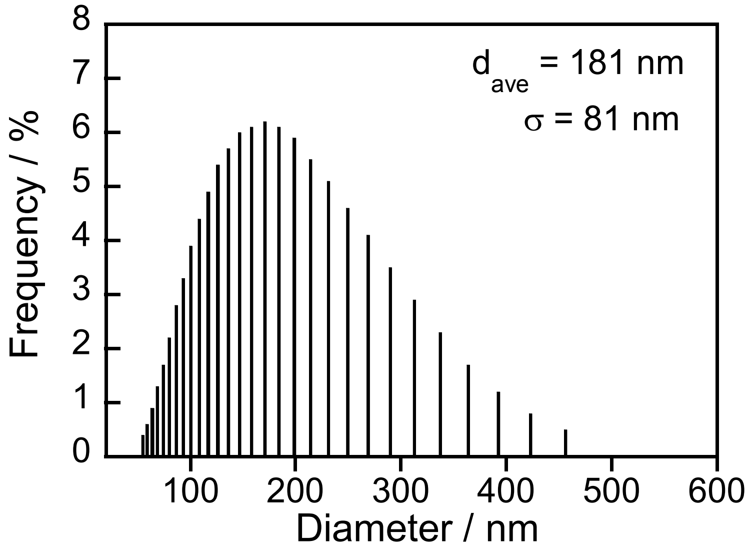

Fig. S4 Size distribution of liposomes composed of DSPC-$AgInTe_2$ composites measured by DLS.

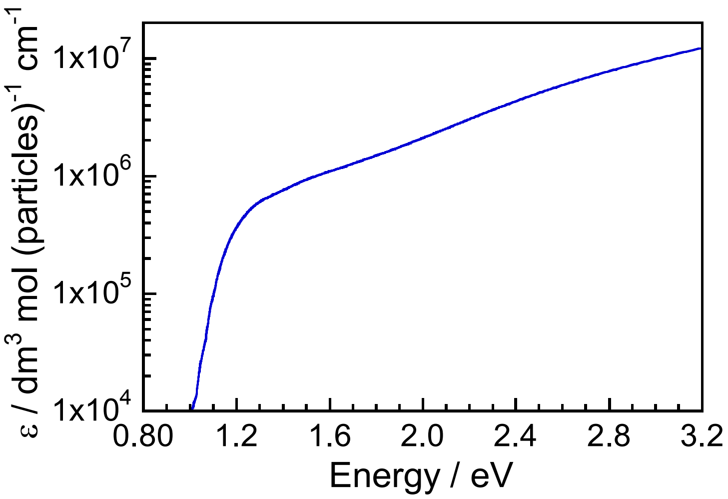

Fig. S5 Molar absorption coefficient (ε) of $AgInTe_2$ NCs at different photon energies. The nanocrystals were prepared at 180°C.

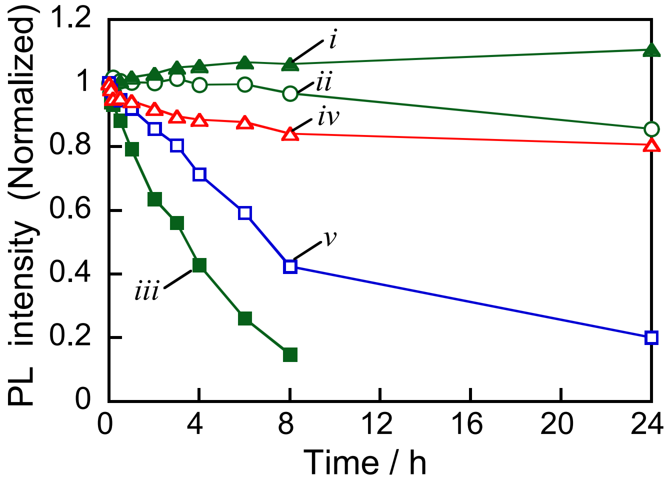

Fig. S6 Changes in PL intensities of DSPC-$AgInTe_2$ NCs composites dissolved in 10 mmol dm^{-3} phosphate buffer solutions during storage under various conditions. Each PL intensity was normalized by the corresponding initial value. The solutions at pH 7.0 were stored in the dark under atmospheres of N_2 (*i*) or air (*ii*), and were continuously irradiated in air by the excitation light with wavelength of 700 nm (the intensity of 17.5 mW cm^{-2}) (*iii*), which were used for the excitation in PL measurements. The durability tests of photoluminescent $AgInTe_2$ NCs in the solutions at pH 5.4 (*iv*) and 8.5 (*v*) was also carried out in air under the dark.

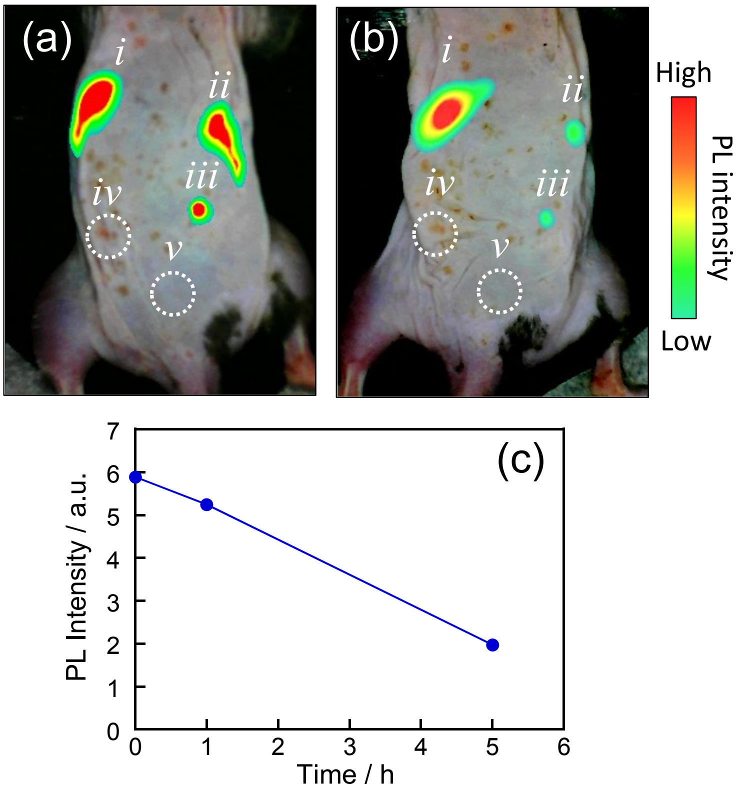

Fig. S7 (a,b) *In vivo* photoluminescence images of mice at (a) 1 h and (b) 5 h after injection of the DSPC-$AgInTe_2$ composite dispersion. A 50 mm^3 portion of DSPC-$AgInTe_2$ dispersion was injected into each site of *i* ~ *v* on the mouse, as shown in the panels a and b. The NC concentrations of the injected solutions were (*i*) 50, (*ii*) 25, (*iii*) 12.5, (*iv*) 6.25, and (*v*) 0 nmol(particles) dm^{-3}. (c) The time course of PL intensity after the injection of the DSPC-$AgInTe_2$ dispersion containing 50 nmol(particles) dm^{-3} $AgInTe_2$ NCs.

References

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