Electronic Supplementary Information

Light-stimulate carrier dynamics of $CuInS_2$/CdS Heterotetrapod Nanocrystals

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Experimental section

Reagents: Oleylamine (80-90%) was purchased from Acros Organics and Aldrich Co. Ltd. and used as received. *N*,*N*-dibutylthiourea (DBTU, 97%) was purchased from Acros Organics and used as received. $Cu(acac)_2$ and CuCl were purchased from Kanto

Chemicals and used as received. In(acac)$_3$ and InCl$_3$ were purchased from Aldrich Co. Ltd. and used as received. Sulfur was purchased from Kanto Chemicals and used as received. Ethanol (99.5%), toluene and chloroform were purchased from Wako Chemicals and used as received.

Synthesis of CuInS$_2$ nanocrystals (NCs): Oleylamine-protected CuInS$_2$ NCs were synthesized according to the previous research.[1,2] First, an *o*-dichlorobenzene solution of oleylamine (8.6 mmol), Cu(acac)$_2$ (1.4 mmol) and In(acac)$_3$ (1.4 mmol) was put in a three-necked flask and heated to 110 °C under an N$_2$ atmosphere. Then, an *o*-dichlorobenzene solution of sulfur (2.4 mmol) previously heated to 110 °C was rapidly injected into the prior solution. The mixture was heated to 180 °C for 1 h and then cooled to room temperature (RT). The obtained NCs were precipitated by using ethanol and then centrifuged. The obtained precipitate was dispersed in chloroform. CuInS$_2$ NCs obtained by present procedure contain much defect and exhibited short lifetime of excited state (6.6 ± 0.9 ps).[2]

Synthesis of CdS/CuInS$_2$ tetrapods: A mixture of CdO (0.23 mmol), tri-*n*-octylphosphine oxide (3.5 mmol), octadecylphosphonic acid (0.43 mmol) and hexadecylphosphonic acid (0.24 mmol) was degassed in a three-necked flask for 60 min at 150 °C under vacuum. The flask was then heated to 320 °C under nitrogen, and then tri-*n*-octylphosphine (2.0 mmol) was added. When the temperature returned to 320 °C, the mixture of CuInS$_2$ NCs (0.02 or 0.04 mmol as Cu or In), sulfur (1.9 mmol) and tri-*n*-octylphosphine (2.0 mmol) were injected all at once. The mixture was heated to 320 °C for 7 min and then cooled to RT. Ethanol was then added to precipitate the heterotetrapods, which were then centrifuged at 7000 rpm for 10 min. The precipitate was dispersed in chloroform. The dispersions were centrifuged again at 7200 rpm for 5 min to remove inadequately capped heterotetrapods. The obtained CdS/CuInS$_2$ tetrapods are shown in Figure S1.

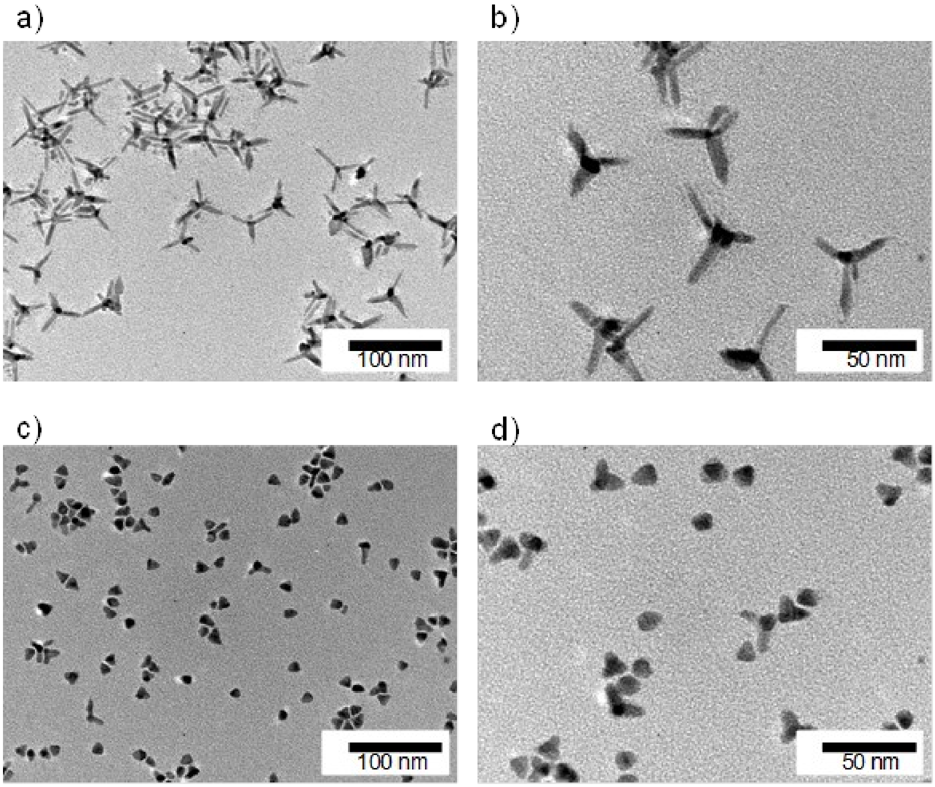

Figure S1. TEM images of $CdS/CuInS_2$ tetrapods synthesized from different loading amount of $CuInS_2$ NCs ((a,b) 0.02 or (c,d) 0.04 mmol as Cu or In).

Characterization: TEM was performed using a JEM1011 (JEOL) at 100 kV. STEM observations were performed using an HD-2300C microscope (HITACHI HIGH-TECHNOLOGIES) equipped with a cold field emission gun and a spherical aberration corrector (CEOS) with an operating voltage of 200 kV. BF-STEM images were simultaneously acquired with DigiScan (GATAN). XRD patterns were taken on a PANalytical X'Pert Pro MPD diffractometer with Cu Kα radiation (λ = 1.542 Å) at 45 kV and 40 mA. UV-vis-NIR absorption spectroscopy was conducted using a U-4100 spectrophotometer (HITACHI). XRF elemental analysis was performed using a JSX-3202C elemental analyzer (JEOL). The absolute photoluminescence quantum yields (QYs) were determined using a Fluolog(r)-3 FL3-2iHR fluorescence spectrometer (HORIBA Jobin Yvon) equipped with PMT (R2658 in the range of UV-Vis-NIR) and InGaAs (Symphony II IGA in the range of NIR-IR) photodetectors, a monochromator, an integrating sphere, and a 450 W xenon lamp. The obtained emission spectra were corrected using a response file that records the sensitivity of the detectors to different wavelengths of light generated using a standard lamp.

Excitation spectrum of heterotetrapod: The emission and excitation spectrum of heterotetrapod was shown in Figure SX. The spectral shape is different at the Vis region from the absorption spectra of tetrapod. It could reflect the different emitting mechanism of $CuInS_2$ excitation and CdS excitation. When CdS was excited, the electron and hole are transfer to C.B. (or donor state) and V.B. (or acceptor state) of $CuInS_2$. The efficiency of carrier transfer affect the intensity of emission, the intensity of excitation spectra at ViS region (i.e. the region, which CdS absorb photons, mainly) diminished.

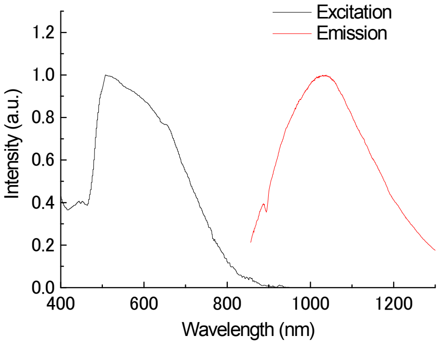

Figure S2. Emission and exciation spectra of $CuInS_2$/CdS heterotetrapod.

Photo-deposition of Rh NCs: First, 0.01 mmol of $CuInS_2$/CdS tetrapods or CdS nanorods (calculated as Cd atoms) was dissolved in toluene (100 uL). An aqueous $RhCl_3$ solution (0.01 mmol) was then added to the solution. Rh^{3+} ions were phase-transferred to the toluene using tetraoctylammonium bromide. Triethylamine (0.5 mmol) was added to the solution as a hole scavenger. The solution was finally irradiated with a light-emitting diode (594 nm, FWHM = 34 nm) for 1 h.

Transient absorption measurements: The femtosecond TA spectroscopy setup used in this study is based on a regenerative amplifier Yb:KGW laser system (pulse width: 300 fs, repetition rate: 50 kHz). TA spectra were measured using white-light probe pulses

(470–1000 nm), generated by illuminating a sapphire crystal with 1030-nm femtosecond pulses from the regenerative amplifier. The remaining power of the regenerative amplifier was used to excite an optical parametric amplifier, which generated the pump pulse with a wavelength of 650 nm. To suppress many-body effects such as Auger recombination, we adjusted the intensity of the pump pulse so that the signal intensities were proportional to the pump intensities. In all measurements, we used solutions of NCs dispersed in $CHCl_3$, contained in a 1-mm-thick quartz cell. All measurements were performed at RT. The recovery time of the bleaching signals in the $CuInS_2$/CdS tetrapods was evaluated by fitting the temporal evolution at 505 or 770 nm using a single exponential function:

$$-\Delta\alpha(t) = Aexp(-\frac{t}{\tau_d}).$$

Here, τ_d is the decay time of the bleaching signals, and A is the amplitude.

Irradiation of the LED to the CdS nanorods in the presence of Rh^{3+}: Irradiating the CdS nanorods with the LED (594 nm) in the presence of Rh^{3+} formed isolated Rh NCs rather than deposited Rh on the CdS rods (Figure S2). This result indicates that the Rh^{3+} ions are not reduced on the surface of the CdS rods because the CdS rods cannot absorb the 594-nm light. The 594-nm light directly excited the Rh^{3+}, forming the isolated Rh NCs. The fact that the selective excitation of the $CuInS_2$ core caused deposition of Rh NCs on the CdS arms is strong evidence that the electron transfer occurred from the conduction band of $CuInS_2$ to that of CdS following the type-II band alignment. Note that the electrons in the conduction bands of $CuInS_2$ or CdS in the tetrapods can transfer to another phase depending on the excitation wavelength.

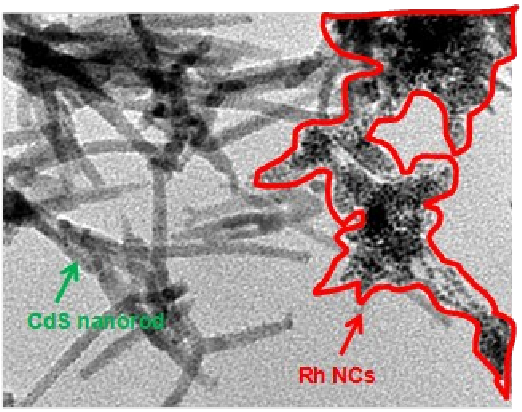

Figure S2. Photo-induced formation of Rh NCs in the presence of CdS nanorods instead of tetrapods (excitation at 594 nm). Isolated Rh NCs formed and aggregated.

References

1. Panthani, M. G.; Akhavan, V.; Goodfellow, B.; Schmidtke, J. P.; Dunn, L.; Dodabalapur, A.; Barbara, P. F.; Korgel, B. A. *J. Am. Chem. Soc.* **2008**, *130*, 16770-16777.
2. Sakamoto, M.; Chen, L.; Okano, M.; Tex, D. M.; Kanemitsu, Y.; Teranishi, T. *J. Phys. Chem. C* **2015**, *119*, 11100-11105.