

## Supplementary Information for

### Crystal Structure-Selective Formation and Carrier Dynamics of Type-II CdS–Cu<sub>31</sub>S<sub>16</sub> Heterodimers

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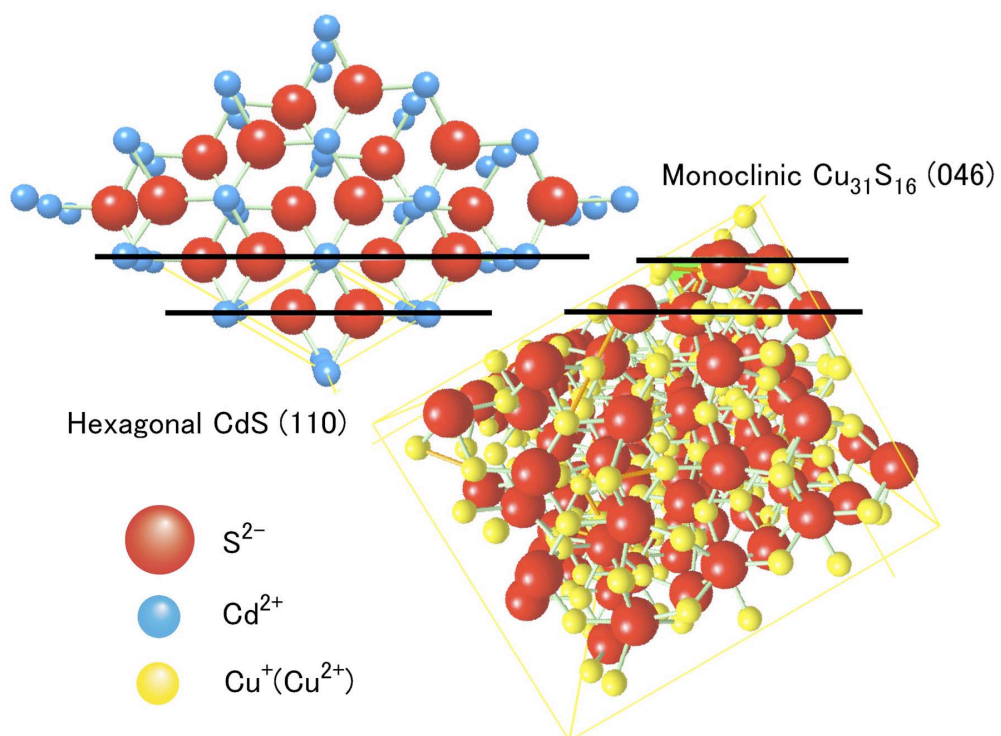
#### Instruments

TEM and HRTEM observations were carried out using JEM1011 (JEOL) at 100 kV and JEM2100F (JEOL) at 200 kV, respectively. XRD patterns were taken on PANalytical X'Pert Pro MPD with CuK<sub>α</sub> radiation ( $\lambda = 1.542 \text{ \AA}$ ) at 45 kV and 40 mA. The UV-Vis-NIR absorption spectroscopy was conducted using a U-4100 spectrophotometer (HITACHI). XRF elemental analysis was carried out using Element Analyzer JSX-3202C (JEOL).

Femtosecond transient absorption was measured using a regenerative amplifier system consisting of a "Hurricane" Ti:sapphire laser (800 nm wavelength, 130 fs fwhm pulse width, 0.75 mJ/pulse intensity, 1 kHz repetition rate) from Spectra Physics. The 800 nm laser light was split into two equal halves, and the first was directed into an optical parametric amplifier (Quantronix, Topas) tuned to give an output at 490 nm used for the pump pulse. The pump pulse was purified of unwanted fundamental laser light and light of other wavelengths by a "cold" NIR cut filter and a short pass filter. Intensity of the pump pulse was 1.5 mW unless otherwise specified in the text. The second half of the fundamental laser light was focused onto a sapphire plate (2 mm thick) to generate a white light continuum for the probe beam. To account for variance in the flux of the probe beam, part of the probe beam was split using a partially transparent mirror (a 1 mm-thick sapphire plate) and the intensity was monitored by a photodiode. The probe beam was focused at the center of the pump beam on the sample and the

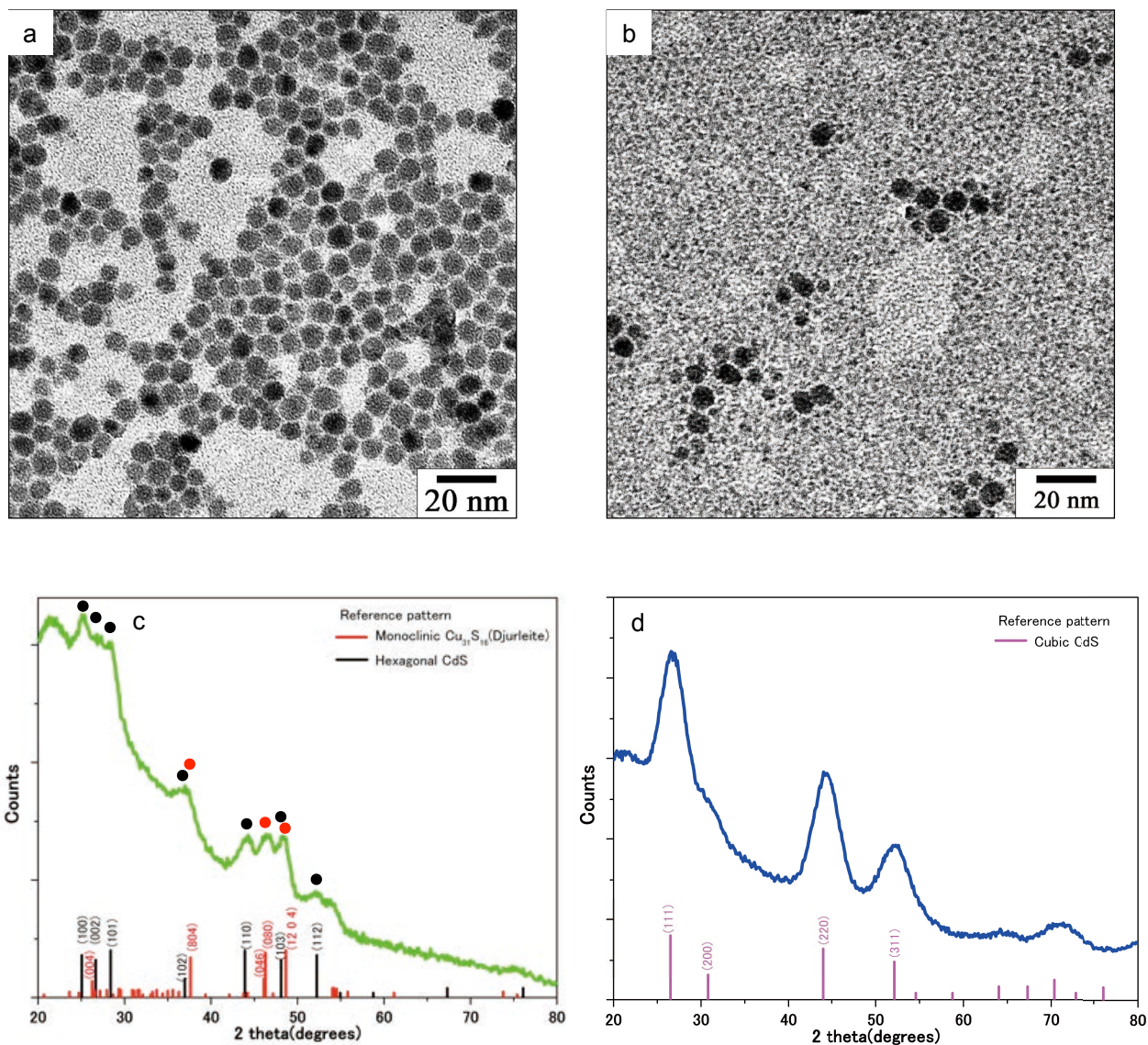
transmitted probe beam was then detected by either a Si or InGaAs detector after passing through a monochromator (Acton Research, SpectraPro-150). A time difference between the arrival of pump and probe beams was achieved using a movable delay stage, and every other pulse of the pump beam was mechanically chopped so that a probe signal with and without pump excitation could be measured. The time resolution of the experiments was approximately 250 fs. Samples were tested at 22°C in air but scanned on a moving platform during experiments to avoid degradation during testing. All results were reproducible over the duration of the experiment and between different samples, suggesting no disturbance to the real transient absorption signal due to photodegradation product buildup.

### Crystal structures of hexagonal CdS phase and monoclinic $\text{Cu}_{31}\text{S}_{16}$ phase



**Figure S1** Crystal structures of hexagonal CdS phase and monoclinic  $\text{Cu}_{31}\text{S}_{16}$  phase. Black lines indicate the CdS (110) plane and  $\text{Cu}_{31}\text{S}_{16}$  (046) planes.

### TEM images and XRD patterns of CdS–Cu<sub>31</sub>S<sub>16</sub> heterodimers and small cubic CdS NPs in supernatant



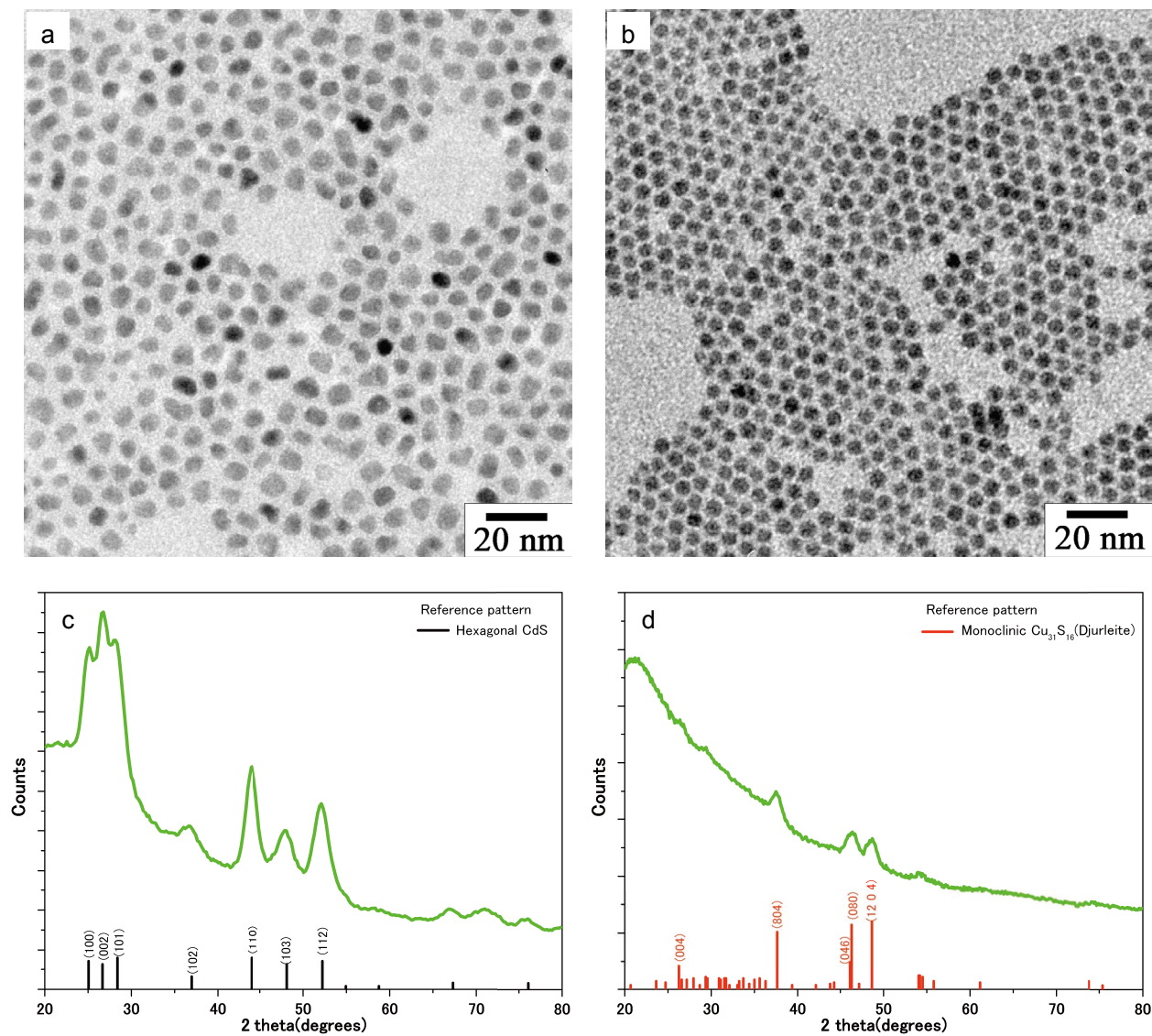
**Figure S2** (a,b) TEM

images and (c,d) XRD patterns of (a,c) CdS–Cu<sub>31</sub>S<sub>16</sub> heterodimers and (b,d) small cubic CdS NPs in supernatant.

Figure S2 shows the TEM images and XRD patterns of CdS–Cu<sub>31</sub>S<sub>16</sub> heterodimers and small CdS NPs in supernatant. The XRD pattern of CdS–Cu<sub>31</sub>S<sub>16</sub> heterodimers exhibited the peaks (black circles) assigned to (100), (002), (101), (102), (110), (103) and (112) planes of the hexagonal CdS and those (red circles) assigned to (804), (080) and (12 0 4) planes of the monoclinic Cu<sub>31</sub>S<sub>16</sub>. The XRD pattern of heterodimers was well agreed with the sum of monoclinic Cu<sub>31</sub>S<sub>16</sub> and hexagonal CdS in *Power Diffraction File* (PDF) (see also Figure S3c

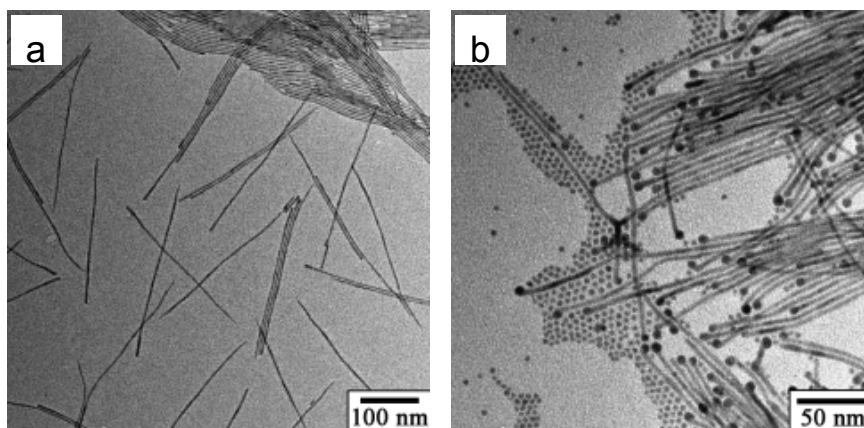
and d), indicating that the heterodimers were composed by both monoclinic  $\text{Cu}_{31}\text{S}_{16}$  and hexagonal CdS segments. On the other hand, the XRD peaks of CdS NPs in supernatant in Figure S2d are assigned to (111), (220) and (311) planes of the cubic CdS. The XRD pattern is well agreed with the reference data of cubic CdS. The above results indicate that the CdS– $\text{Cu}_{31}\text{S}_{16}$  heterodimers were formed by the selective seeded growth of  $\text{Cu}_{31}\text{S}_{16}$  on preformed hexagonal CdS NPs.

### TEM images and XRD patterns of hexagonal CdS NPs and monoclinic $\text{Cu}_3\text{S}_{16}$ NPs



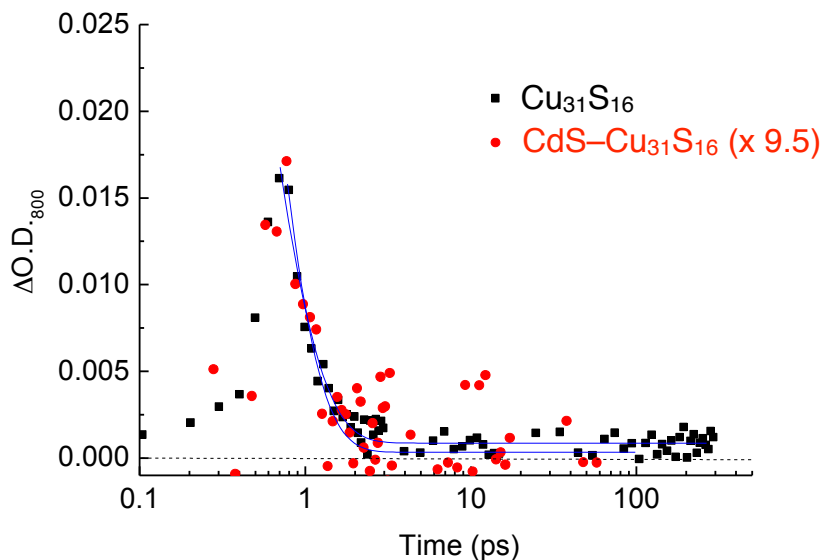
**Figure S3** (a,b) TEM images and (c,d) XRD patterns of (a,c) hexagonal CdS NPs and (b,d) monoclinic  $\text{Cu}_3\text{S}_{16}$  NPs synthesized as references.

**TEM images of hexagonal CdS nanowires and CdS–Cu<sub>2-x</sub>S heterostructures**



**Figure S4** TEM images of (a) hexagonal CdS nanowires and (b) CdS–Cu<sub>2-x</sub>S heterostructures.

### Kinetic traces of laser-pulse induced transient absorption of $\text{Cu}_{31}\text{S}_{16}$ NPs and $\text{CdS-Cu}_{31}\text{S}_{16}$ heterodimers



**Figure S5** Kinetic traces of laser-pulse (490 nm) induced transient absorption of  $\text{Cu}_{31}\text{S}_{16}$  NPs (black) and  $\text{CdS-Cu}_{31}\text{S}_{16}$  heterodimers (red).

Excited  $\text{Cu}_{31}\text{S}_{16}$  exhibited broad absorption from Vis to IR region peaks at around 550 nm, which is attributed to the absorption of the carrier trapping.<sup>1</sup> The decay curves of transient absorption of  $\text{Cu}_{31}\text{S}_{16}$  NPs at 800 nm were well-fitted by the single exponential decay function and the lifetimes were estimated to be 0.40 ps (Fig. S5). The difference in intensity of the transient absorption might be caused by the different concentrations between the  $\text{Cu}_{31}\text{S}_{16}$  NPs and the  $\text{CdS-Cu}_{31}\text{S}_{16}$  heterodimers. Previously, Mehra and Zhang et al. measured the decay profile of laser-induced transient absorption of PVP-protected  $\text{Cu}_2\text{S}$  at 790 nm and estimated the life times (double exponential decay function, fast and slow components were 1.1 ps and component longer than the limited window of fs-laser flash photolysis system ( $> 80$  ps), respectively).<sup>2</sup> Xu and Han et al. reported the lifetime of excited  $\text{Cu}_{1.94}\text{S}$  nanodisks to be 1.41 ps and component longer than the limited window of fs-laser flash photolysis system ( $> 30$  ps).<sup>3</sup> The lifetime of excited  $\text{Cu}_{31}\text{S}_{16}$  was significantly shorter than those of previously reported values. It is suggested that the energy transfer to localized surface plasmon and/or Auger type recombination would reduce the lifetime of exciton generated in  $\text{Cu}_{31}\text{S}_{16}$  NPs.<sup>4</sup> In the case of  $\text{CdS-Cu}_{31}\text{S}_{16}$  heterodimers, the decay profile of transient absorption at 800 nm was quite similar to that of  $\text{Cu}_{31}\text{S}_{16}$  NPs, inferring that the vacancy-induced decay process from excited  $\text{Cu}_{31}\text{S}_{16}$  phase in heterodimer (*i.e.*, energy transfer to localized surface plasmon and/or Auger type recombination) is predominant comparing with the energy or electron transfer to CdS phase.



## References

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