## Supplementary Information for

# Pseudomorphic amorphization of three-dimensional superlattices through morphological transformation of nanocrystal building blocks

Masaki Saruyama,<sup>1</sup>\* Ryo Takahata,<sup>1</sup> Ryota Sato,<sup>1</sup> Kenshi Matsumoto,<sup>1</sup> Zhu Lingkai,<sup>2</sup> Yohei Nakanishi,<sup>1</sup> Motoki Shibata,<sup>3</sup> Tomotaka Nakatani,<sup>3</sup> So Fujinami,<sup>3</sup> Tsukasa Miyazaki,<sup>3</sup> Mikihito Takenaka<sup>1</sup> and Toshiharu Teranishi<sup>1,2</sup>\*

<sup>1</sup> Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

<sup>2</sup> Graduate School of Science, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

<sup>3</sup> Office of Society-Academia Collaboration for Innovation, Kyoto University, Yoshida-

Honmachi, Kyoto 606-8501, and Gokasho, Uji, Kyoto 611-0011, Japan

e-mail: saruyama@scl.kyoto-u.ac.jp, teranisi@scl.kyoto-u.ac.jp

### Methods

### <u>Chemicals</u>

CuCl<sub>2</sub>·2H<sub>2</sub>O (>99.0%, FUJIFILM Wako Chemicals), dodecylamine (DDA, >97.0%, Tokyo Chemical Industry), 1-dodecanethiol (DDT, >98%, Sigma-Aldrich), and *tert*-dodecanethiol (*t*-DDT, >98%, Sigma-Aldrich) were used as received without purification.

### Synthesis of 3D Cu<sub>2</sub>S nanocrystal (NC) superlattices (SLs)

A mixture of CuCl<sub>2</sub>·2H<sub>2</sub>O (1 mmol) and DDA (10 mL) was placed in a three-necked flask, which was vacuumed, and heated to 80 °C to remove hydrated water of CuCl<sub>2</sub>·2H<sub>2</sub>O. After the flask refilled with N<sub>2</sub>, DDT (1 mL) was injected, the color of the solution turned from darkblue to cloudy light-yellow due to the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> and the formation of the Cu-DDT complex. The solution was heated to 230 °C at 10 °C min<sup>-1</sup> and kept at 230 °C for the desired times. After the solution cooled to room temperature, poor solvent (35 mL) was added, and the mixture was kept undisturbed in a 50-mL centrifugation tube until most of the powdery product precipitated. The supernatant was discarded and this step was repeated twice. As poor solvents, ethanol was used in the first two cycles and acetone was used in the final cycle. The purified product, a powder, was stored in acetone. The control experiment using *t*-DDT was carried out in the same way, except DDT was replaced with *t*-DDT and the final temperature was changed to 200 °C. The reaction was quenched 0–90 s after reaching 200 °C by immersing the reaction flask in a water bath.

### Characterization

Transmission electron microscopy (TEM) images were obtained using HT7820 (HITACHI). High-resolution TEM (HRTEM) and selected-area electron diffraction (SAED) measurements were conducted using JEM-ARM200F (JEOL). Scanning electron microscopy (SEM) observation was carried out on a S-4800 (HITACHI). SEM images at high magnification (Figure 1e-h) were denoised by removing spots of periodic noises in corresponding FFT images. Focused ion beam (FIB) SEM operation was carried out using Ethos NX5000 (HITACHI). X-ray diffraction (XRD) patterns were measured using X'Pert Pro MPD (Panalytical) with CuK $\alpha$  radiation ( $\lambda$  = 1.542 Å) operated at 45 kV and 40 mA. Ex situ smallangle X-ray scattering (SAXS) measurements were carried out using Nano-viewer (Rigaku) with CuK $\alpha$  radiation ( $\lambda$  = 1.542 Å) operated at 40 kV and 30 mA, as well as using the BL28XU beamline of SPring-8; the X-ray photon energy, camera length, and X-ray beam size at the sample position (horizontal × vertical) were 18 keV ( $\lambda$  = 0.6889 Å), 2972 mm, and 200  $\mu$ m × 200 µm, respectively. The camera length was calibrated using the standard Ag behenate reference. The scattered intensities were expressed as a function of the scattering vector,  $q = (4\pi \sin \theta)/\lambda$ , where  $2\theta$  is the scattering angle relative to the incident beam. Visible (vis)-near-infrared (NIR) extinction spectra and diffusion reflectance spectra (DRS) were obtained using U-4100 (HITACHI). To prepare samples for diffusion reflectance measurements, thin films of Cu<sub>2</sub>S NC SLs were formed by depositing acetone dispersions of Cu<sub>2</sub>S NC SLs on synthetic quartz substrates, followed by drying.

#### In situ SAXS measurements

The colloidal synthesis was reproduced in the BL40B2 beamline of SPring-8 with a custommade glass reactor with a  $\Phi$ 10-mm X-ray window (Figure S6). The thickness of the solution between the windows was 4 mm. The reactor was wrapped with a ribbon heater to keep the X-ray window uncovered, and it was connected to a vacuum pump and a N<sub>2</sub> gas container. The X-ray photon energy was set to 17.5 keV ( $\lambda$  = 0.7086 Å), and the beam spot size was 250 µm × 40 µm. The X-ray transmittance of the reactor was ~20%. SAXS patterns were collected by the Pilatus3S 2M detector every 12 s, including 10-s accumulation with 2-s intervals between each frame. The obtained 2D SAXS images were integrated into 1D scattering curves using the Fit2D software (ver. V17.006).<sup>1</sup> The camera length, calculated using the standard Ag behenate reference, was 3219 mm.

SAXS pattens from dispersed NCs were fitted with the NanoSolver software (Rigaku, ver. 3.7.6.0). Curves were fitted with the theoretical scattering intensity of non-uniform sized NCs [I(q, R, M)]:

$$I(q, R, M) = K \langle F_{sphere}(q) \rangle^2$$

$$F_{sphere}(q) = \Delta \rho \cdot \frac{4\pi}{q^3} \left( \sin(qR) - qR\cos(qR) \right)$$
$$\langle F_{sphere}(q) \rangle^2 = \int_0^\infty F_{sphere}(q)^2 P_{R_0}^M(R) \, dR$$
$$P_{R_0}^M(R) = \frac{1}{\Gamma(M)} \left(\frac{M}{R_0}\right)^M e^{-\frac{MR}{R_0}R^{-1+M}}$$
$$\sigma = \frac{1}{\sqrt{M}} \times 100$$

Where *K* is a constant that is a function of the type of radiation used, the product of the number of scatterers, and the sample properties,  $F_{sphere}(q)$  is the spherical form factor,  $P_{R_0}^M(R)$  is the gamma distribution function, *R* is the NC radius,  $\Delta \rho$  is the scattering contrast, *v* is the single NC volume, *M* is the distribution coefficient,  $R_0$  is the average NC radius, and  $\sigma$  is the relative size distribution of NCs (%).

#### Calculation of the interaction forces between Cu<sub>2</sub>S NCs

The van der Waals (vdW) force between Cu<sub>2</sub>S cores and steric repulsion between DDT ligands were considered as the interaction forces between two DDT-coated-Cu<sub>2</sub>S NCs.<sup>2–4</sup> Each force was calculated as follows.

The vdW force between two Cu<sub>2</sub>S cores is given by

$$U_{vdW} = -\frac{A}{3} \left[ \frac{r^2}{4rd_i + d_i^2} + \frac{r^2}{(2r+d_i)^2} + \frac{1}{2} \ln \frac{4rd_i + d_i^2}{(2r+d_i)^2} \right],$$

where *A* is the Hamaker constant of Cu<sub>2</sub>S, *r* is the radius of Cu<sub>2</sub>S cores, and  $d_i$  is the center-to-center interparticle distance. *A* was assumed to be  $3.0 \times 10^{-19}$  J considering the Hamaker constant of typical metals (2–5 × 10<sup>-19</sup> J) and metal sulfides (1–2 × 10<sup>-19</sup> J).

The steric repulsion force between DDT ligands on spherical Cu<sub>2</sub>S NCs is given by

$$U_{steric} = \frac{k_B T \pi^3 \sigma r L_0^3}{120 N b^2} (-45 - 30 \ln u + 54u - 10u^3 + u^6), \qquad u \equiv \frac{d_i}{2L_0}$$

where  $\sigma$  is the grafting density of DDT (7.0 × 10<sup>18</sup> m<sup>-2</sup>),  $L_0$  is the full length of DDT (1.8 × 10<sup>-9</sup> m), *b* is the Kuhn length of DDT, and *N* is the number of *b* per DDA.  $Nb^2$  is defined as the square average end-to-end distance of DDT (2.0 × 10<sup>-17</sup> m<sup>2</sup>).<sup>2</sup> The calculation result is shown in Figure S8.

## Cu-DDT complex

The Cu-DDT precursor was collected as a white powder from the reaction solution before the nucleation of NCs. The SEM image (Figure S1b) showed flower-like microparticles made of Cu-DDT nanosheets. The SAXS pattern of Cu-DDT showed a peak at 3.55 nm (Figure S1c) corresponding to the interlayer distance of the Cu-DDT lamellar structure (Figure S1a).<sup>5</sup> In the *in situ* SAXS measurement, the intensity of this peak decreased as the temperature increased from 135 °C because the lamellar structure melted (Figure S1d).



**Figure S1.** (a) Schematic structure of lamellar Cu-DDT. (b) SEM image and (c) *ex situ* SAXS pattern of the Cu-DDT complex. (d) Temperature-dependent *in situ* SAXS peak intensity of Cu-DDT at q = 1.754 nm<sup>-1</sup>.



**Figure S2**. XRD patterns of the products obtained by holding the reaction temperature at 230 °C for various reaction times and the Cu-DDT complex.



**Figure S3.** Lower magnification SEM image of polyhedral Cu<sub>2</sub>S NC SLs at 10 min after reaching the reaction temperature of 230 °C.



Figure S4. SEM image of disk-shaped Cu<sub>2</sub>S NCs at 35 min after reaching the reaction temperature of 230  $^{\circ}$ C.



**Figure S5.** (a) HRTEM image of disassembled spherical Cu<sub>2</sub>S NCs (10 min). (b) FFT pattern of Cu<sub>2</sub>S NC marked by the orange square in (a). (c) Unit cell model of low-chalcocite Cu<sub>2</sub>S seen from the [010] zone axis. (d) HRTEM image of individual disk-shaped Cu<sub>2</sub>S NCs (35 min) with face-down orientation. (e) FFT pattern of (d). (f) Unit cell model of low-chalcocite Cu<sub>2</sub>S seen from the [ $\overline{1}$ 02] zone axis. (g) HRTEM image of disk-shaped Cu<sub>2</sub>S NCs (35 min) with edge-up orientation. (h) Crystal model of disk-shaped Cu<sub>2</sub>S NC. These observations indicate that initially formed spherical Cu<sub>2</sub>S NCs preferentially grow in the lateral direction, such as [060] and [630], to form disk-shaped Cu<sub>2</sub>S NCs with { $\overline{2}$ 04} basal planes.



Figure S6. Photographs of the custom-made reaction flask. (Left) front and (right) side views.



**Figure S7.** Background-subtracted *in situ* SAXS patterns at the reaction times of 10.0 min and 11.0 min (red open circles) and fitting curves (black lines).



**Figure S8.** (a) Schematic model of two possible interparticle forces. (b) Interaction potentials between two DDT-capped-Cu<sub>2</sub>S NCs with various diameters (2*R*) as a function of interparticle distance ( $d_i$ ). (b) Potential local minimum values between two Cu<sub>2</sub>S NCs as a function of NC diameter.



**Figure S9.** Non-normalized, background-subtracted *in situ* SAXS patterns after the selfassembly started. The intensity of diffusion scattering from dispersed Cu<sub>2</sub>S NCs rapidly decreased (as indicated with an arrow) as the concentration of disassembled Cu<sub>2</sub>S NCs in the solution decreased.



**Figure S10.** Time evolved (black) lattice constant of *fcc*  $Cu_2S$  NC SLs and (blue) center-tocenter interparticle distance estimated by the positions of sharp peaks in *in situ* SAXS experiment. (Red)  $Cu_2S$  core diameter assuming that surface-to-surface interparticle distance is 2.5 nm.



**Figure S11.** Temporal evolution of *in situ* SAXS patterns after the self-assembly started. Solid triangles indicate the broad shoulder peak emerging near the 111 diffraction peak.



**Figure S12.** (Left) low- and (right) high-magnification SEM images of "faceted" disordered Cu<sub>2</sub>S NC SLs (35 min after reaching 230 °C). Scale bars = (left) 5  $\mu$ m and (right) 0.5  $\mu$ m.



**Figure S13.** (a–c) (upper) SEM and (lower) TEM images of the columnar assembly of diskshaped Cu<sub>2</sub>S NCs formed by holding the reaction temperature at 200 °C for (a) 0 s, (b) 60 s and (c) 90 s in the synthesis using *t*-DDT instead of DDT. (d) SAXS pattern and schematic structure of the powdery product in (c). (e) Contour plot of (left) in situ SAXS pattern and (right) temperature profile over the reaction time during the reaction using *t*-DDT. (f) Schematic illustration of the overall process of the structural evolution of Cu<sub>2</sub>S NC SLs synthesized using *t*-DDT.



**Figure S14.** (a) Evolution of *in situ* SAXS patterns in the reaction using *t*-DDT. (b) TEM image of the product after the *in situ* SAXS experiment.

### References

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