Electronic Supplementary Material (ESI) for Faraday Discussions.

Electronic Supplementary Information for

# Determination of a localized surface plasmon resonance mode of $Cu_7S_4$ nanodisks by plasmon coupling

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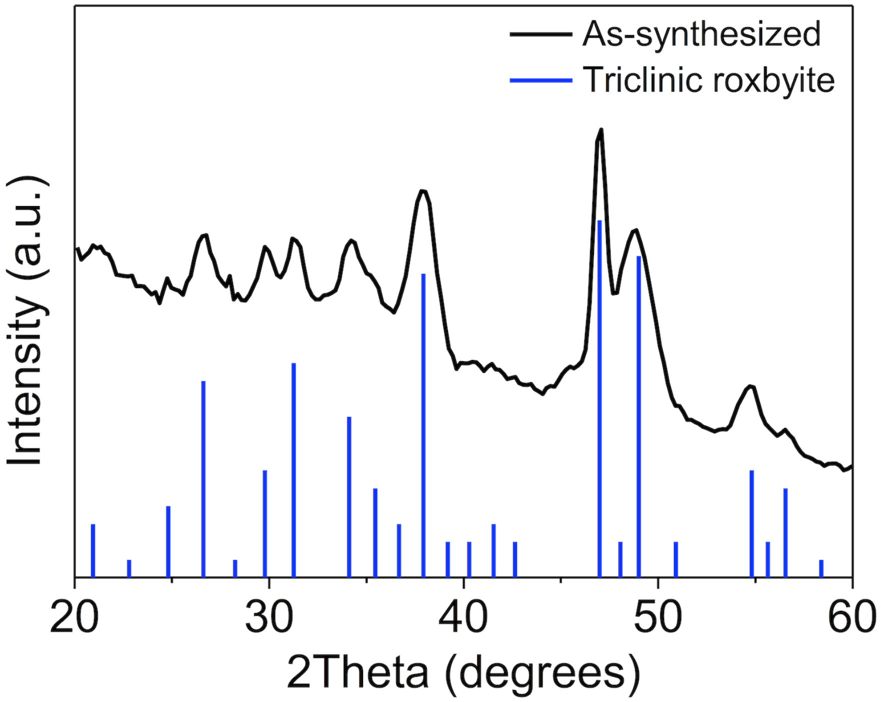

**Figure S1.** (a) XRD pattern of as-synthesized $Cu_7S_4$ nanodisks with reference data of triclinic roxbyite $Cu_{58}S_{32}$.[1] The diffraction pattern of monoclinic $Cu_7S_4$ phase identified in our previous report[2] is approximately the same as that of triclinic $Cu_{58}S_{32}$ phase. Thus, the crystal structure of monoclinic $Cu_7S_4$ is equal to triclinic $Cu_{58}S_{32}$.

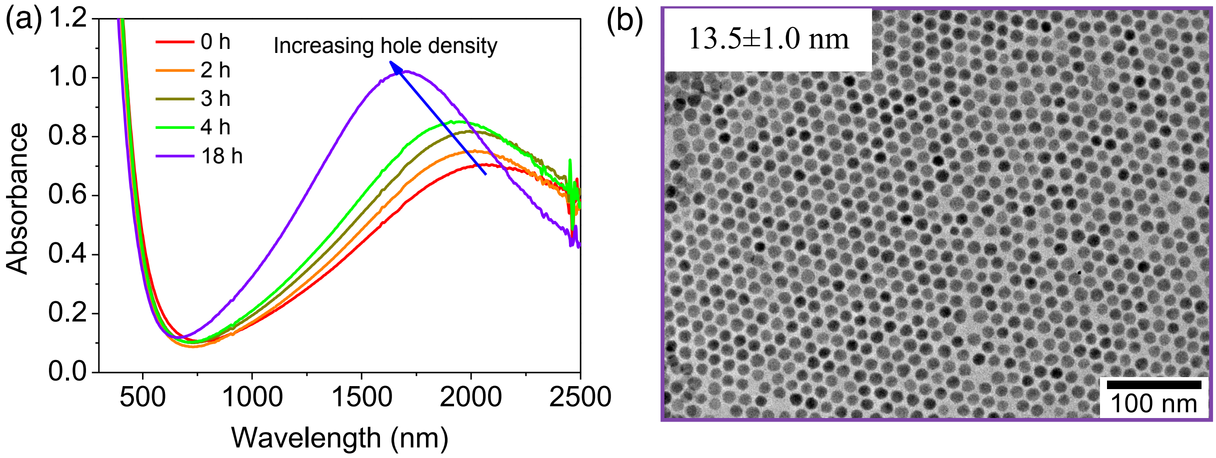

**Figure S2.** (a) Time evolution of UV-Vis-NIR absorption spectra of as-synthesized Cu$_7$S$_4$ nanodisks in toluene during oxidation with air. (b) TEM image of oxidized (oxidation for 18 h) Cu$_7$S$_4$ nanodisks oxidized for 18 h. The Cu$_7$S$_4$ nanodisks stored in a glovebox were diluted and transferred to 5-mL flask, stabilized by a trace amount of OAm, taken out from a glovebox, and oxidized under air exposure without magnetic stirring. The slight decrease in size is due to the formation of Cu:OAm complexes.

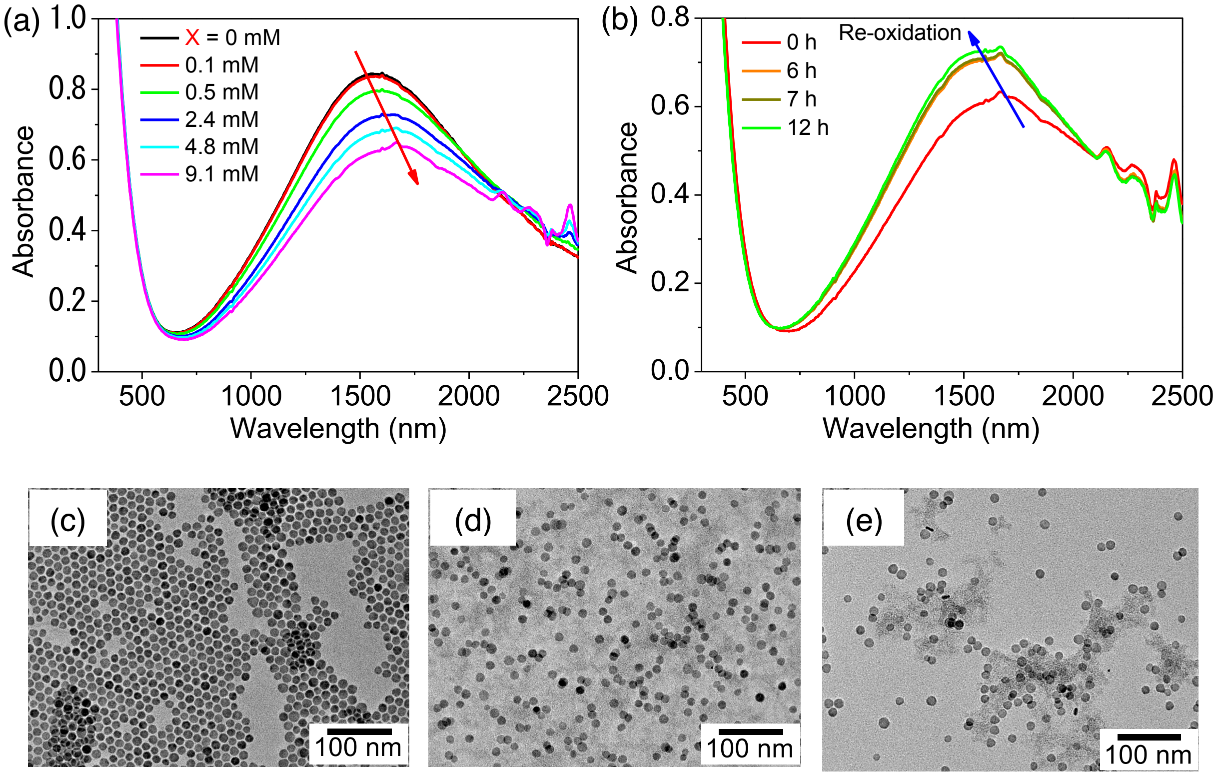

**Figure S3.** (a) UV-Vis-NIR absorption spectra of oxidized $Cu_7S_4$ nanodisks in toluene (a) after reduction with various amounts of DIBAH for 5min and (b) after subsequent re-oxidation with air. TEM images of (c) air oxidized, (d) DIBAH reduced and (e) air re-oxidized $Cu_7S_4$ nanodisks. The shape and size of $Cu_7S_4$ nanodisks were conserved during the oxidation and reduction. Reduction with DIBAH: in a glovebox, 10 mL of oxidized nanodisks in toluene was transferred to a glass vial. Then, 0.1 M DIBAH toluene solution was stepwise added and shaken for 5 min. A total volume of 1.0 mL of DIBAH toluene solution was added. Re-oxidation with air: in a glovebox, the reduced $Cu_7S_4$ nanodisks were transferred to 5-mL volumetric flask, taken out from a glovebox and oxidized under air exposure without magnetic stirring.

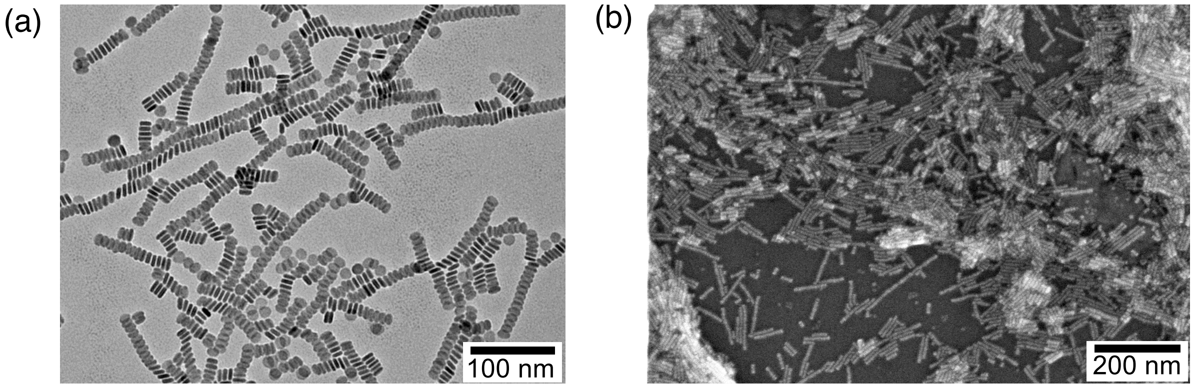

**Figure S4.** (a) TEM and (b) SEM images of the $Cu_7S_4$ nanodisk arrays.

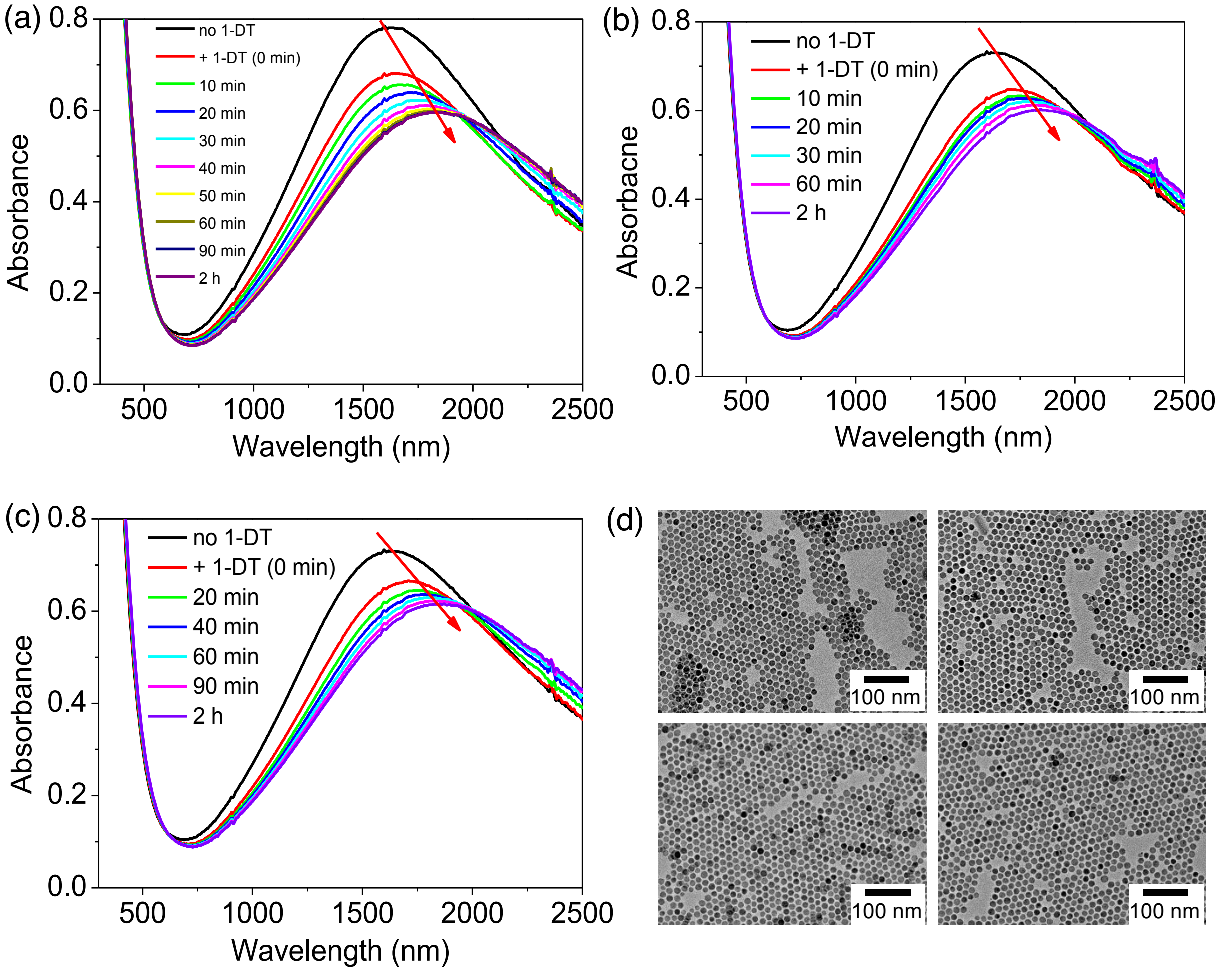

**Figure S5.** Time evolution of UV-Vis-NIR absorption spectra of oxidized $Cu_7S_4$ nanodisks in $CHCl_3$ (5 mL) after an addition of (a) 100 μL of 0.1 M 1-DT $CHCl_3$ solution (including 10 μmol 1-DT), (b) 100 μL of 1.0 M 1-DT $CHCl_3$ solution (including 100 μmol 1-DT), and (c) 1-DT (80 μmol) and shaken for 30 min. All the experiments were conducted in a glovebox. (d) TEM images of $Cu_7S_4$ nanodisks (top left) oxidized by air, (top right), reduced by 10 μmol 1-DT, (bottom left) 100 μmol 1-DT, and 80 μmol of pure 1-DT (bottom right). For TEM observation, samples after 2 h reduction by 1-DT were dried in glovebox. The shape and size of the $Cu_7S_4$ nanodisks are preserved after reduction. The increase of 1-DT concentration does not trigger the formation of nanodisk arrays.

## Calculation of amount of 1-DT required to completely cover the hexagonal {100} facets of nanodisks

We roughly calculated the amount of 1-DT required to completely cover the hexagonal facets of $Cu_7S_4$ nanodisks as follows. First, we calculated the surface area of a hexagonal {100} facet ($S_{\mathrm{disk}}$) of the $Cu_7S_4$ nanodisk to be 127 $\mathrm{nm}^2$ as a regular hexagon. A volume of a single nanodisk ($V_{\mathrm{disk}} = 573\ \mathrm{nm}^3$) was obtained as the $S_{\mathrm{disk}}$ value and its thickness. According to the previous work, the crystal structure of roxbyite $Cu_{58}S_{32}$ is triclinic (see details in Figure S6).[1] Because the structure of a unit cell is similar to the cuboid, the volume of a unit cell ($V_{\mathrm{unit\ cell}}$) can be calculated to be 2.79 $\mathrm{nm}^3$ by the following formula,

$$V_{\mathrm{unit\ cell}} = a \times b \times c$$

The number of Cu atoms in a single nanodisk ($N_{\mathrm{Cu,\ disk}}$) is calculated to be $2.38 \times 10^4$ according to the following formula,

$$N_{\mathrm{Cu,\ disk}} = (V_{\mathrm{disk}} / V_{\mathrm{unit\ cell}}) \times N_{\mathrm{Cu,\ unit\ cell}}$$

where $N_{\mathrm{Cu,\ unit\ cell}}$ is the number of Cu atoms in a unit cell ($58 \times 2 = 116$). The concentration of Cu atoms in the whole $Cu_7S_4$ nanodisks in Figure 5c was estimated to be 24.5 mM from the O.D. Thus, the number of $Cu_7S_4$ nanodisks ($N_{\mathrm{disk}}$) in 5.0 mL of $CHCl_3$ solution is calculated to be $3.1 \times 10^{15}$ by the following equation,

$$N_{\mathrm{disk}} = (5.0 \times 10^{-3} \times 24.5 \times 10^{-3} \times N_{\mathrm{A}}) / N_{\mathrm{Cu,\ disk}}$$

Where $N_{\mathrm{A}}$ is the Avogadro's constant. The total surface area of the hexagonal facets of $Cu_7S_4$ nanodisks ($S$) was estimated to be $7.9 \times 10^{17}\ \mathrm{nm}^2$ from the following equation,

$$S = 2 \times S_{\mathrm{disk}} \times N_{\mathrm{disk}}$$

Figure S6 shows that ten Cu atoms are exposed on the (100) facet with the area of 2.08 $nm^2$ in a unit cell of roxbyite. When we assume that one 1-DT molecule is adsorbed to a single Cu atom on {100} planes, the maximum amount of 1-DT adsorbed on the hexagonal facets is roughly estimated to be 6.3 μmol.

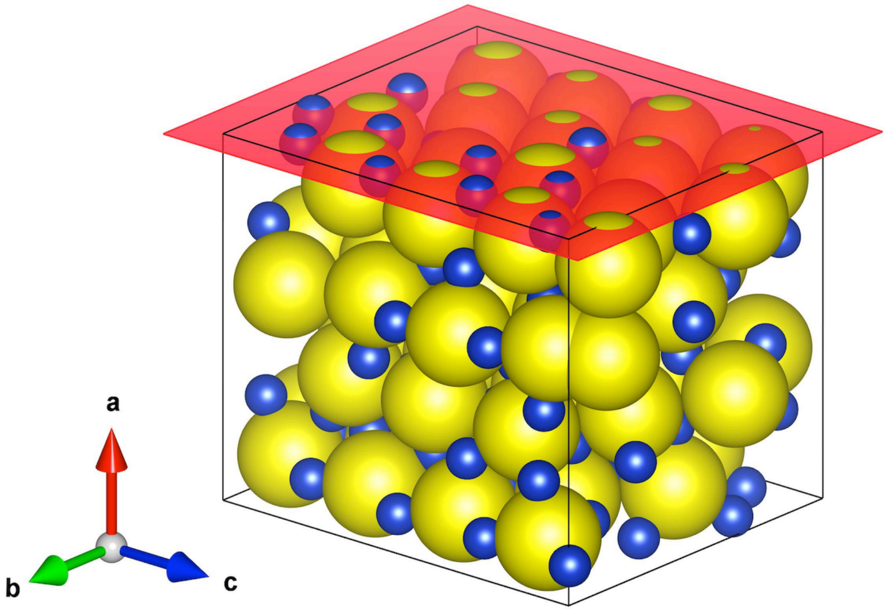

**Figure S6.** Unit cell of triclinic roxbyite $Cu_{58}S_{32}$ as ideal formula. Cu cations and S anions are shown in small blue spheres and large yellow spheres, respectively. The detailed crystal structure is as follows: $a$ = 13.4051(9), $b$ = 13.4090(8), $c$ = 15.4852(3) Å; $\alpha$ = 90.022(2), $\beta$ = 90.021(2), $\gamma$ = 90.020(3)°; $Z$ = 2.[1] The translucent red plane represents the (100) plane.

## References

1 W. G. Mumme, R. W. Gable and V. Petříček, *Can. Mineral.* 2012, **50**, 423–430.

2 M. Kanehara, H. Arakawa, T. Honda, M. Saruyama and T. Teranishi, *Chem. Eur. J.* 2012, **18**, 9230–9238.