# Nonlinear optical absorption and ultrafast carrier dynamics of copper

# antimony sulfide semiconductor nanocrystals

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#### 1. Fabrication of the CuSbS NCs

#### Chemicals:

Oleylamine (OLA,  $C_{18}H_{37}N$ , 80–90%), N,N'-diphenylthiourea (DPT,  $C_{13}H_{12}N_2S$ , 98%), diphenyl ether (>99%), Copper(I) iodide (CuI,  $\geq$ 99.5%), and antimony(III) chloride (SbCl<sub>3</sub>, 99.9%) were purchased from Aladdin. All chemicals were used without any further purification.

## Methods:

# Preparation of sulfide precursor:

2.2831 g (10 mmol) DPT and 10 mL diphenyl ether were mixed in a 20 mL flask and heated at 120-150 °C under atmosphere until the complete dissolution of DPT (about 15-30 min). Since DPT would precipitate out of diphenyl ether at room temperature, the sulfide precursor solution needs to be pre-heated to 120 °Cbefore injection.

## Preparation of CAS QDs:

The preparation process of CuSbS NCs is investigated in our previous work[1, 2]. A typical hot-injection method was employed for the preparation of CAS QDs. Briefly, CuI and 30 mL OLA were mixed in a 50 mL three-nick flask. Whereafter, the mixture were heated to 130 °C under Ar atmosphere. SbCl<sub>3</sub> was added into the solution after the dissolution of CuI, and then a clear slight yellow solution would be achieved. Then, the sulfide precursor was swiftly injected into the above solution. The mixture was cooled down to room temperature after 5 min. Afterwards, 1 mL the reaction solution was mixed with 3 mL methanol and centrifuged at 8000 rpm for 3 min. 4 mL hexane was employed to redisperse the QDs after the suspension was discarded, and then

centrifuged at 8000 rpm for another 3 min. Finally, the precipitate was discarded to obtain the QDs solution. The precursors ratio of Cu:Sb:S were set as 1:1:3, 3:1:4.5, and 3:1:8 for the preparation of CuSbS<sub>2</sub>, Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>, and Cu<sub>3</sub>SbS<sub>4</sub>, respectively.

#### <u>Characterization:</u>

The crystal structures and microstructures of CAS QDs were characterized by XRD with Cu K $\alpha$  radiation (Bruker D8 Advance powder X-ray diffractometer), and TEM (JEM-3100, JEOL, Japan). Energy dispersive spectroscopy (EDS) data were collected as an ensemble measurement in a field emission scanning electron microscope (FESEM, JSEM-5610LV). The steady-state absorption spectra was measured with a UV-VIS-IR spectrometer (Cary 5000, AGILENT).

#### 2. Details of the fs-resolved pump-probe system

1. Transient absorption signal

$$\Delta A = A_{ex} - A_0 = \lg(I_{00} / I_{ex}) - \lg(I_{00} / I_0) = \lg(I_0 / I_{ex})$$

Where,  $\Delta A$  is the absorption difference,  $A_{ex}/A_0$  are the absorptance with/without the pump light,  $I_{ex}/I_0$  are the intensity of the probe intensity of the probe light after the sample when the pump light is on/off.

# 2. Instrument response function

The instrument response function (IRF) is a very short response around the time zero. In this work, it is measured by conducting pump-probe measurements on n-hexane in a quart cuvette, with optical pathlength of 1 mm. The pump was the second harmonic of the laser  $\lambda$ = 400 nm. The probe continuum was generated from the fundamental 800 nm beam injecting into a CaF<sub>2</sub> crystal. A cross-correlation signal occurs when the pump and probe pulses overlap at time zero point. To obtain the IRF, the kinetic profiles at several probe wavelengths were fitted with the Gaussian function and its first and second derivatives, according to the following equation:

$$y(t) = \exp\left[-\left(\frac{t-t_0}{t_p/1.67}\right)^2\right] * \left(A+Bt+Ct^3\right)$$

Where,  $t_0$  is the time zero (point of the signal sign inversion),  $t_p$  is the Instrument response time, which corresponds to the full width at half maximum (FWHM) of the convolution of two pulses with a Gaussian shape. It is not a constant, and closely dependent on the probe wavelength varies. Besides, peak position varies with the probe wavelength, owing to the dispersion. Under the condition of  $\lambda$ pump=400 nm, Ppump=1mW, the IRF was listed in table S1.

Wavelength/	346.1	360.5	443.3	449.1	457.9	469.5	475.4	499.4	525.2	548.7	598.4	623.3	648.3	672.2
nm														
t <sub>0</sub> /ps	0.1634	0.3503	1.171	1.286	1.246	1.345	1.376	1.442	1.555	1.721	1.871	1948	2.206	2.080
t <sub>p</sub> (FWHM)/ps	0.2267	0.1189	0.1886	0.1310	0.0839	0.2006	0.2270	0.1996	0.2272	0.3058	0.3617	0.3921	0.4334	0.4953

Table S1. IRF versus the probe wavelength



Figure S1. IRF versus probe wavelength.

3. Dispersion correction

As broad band white continuum going through the 1-mm-optical length solvent, Normal group velocity dispersion (GVD), that is to say, the red light moves faster than the blue one when the probe white light moves along the CuSbS solution[3]. As a result, the time zero of the TA signal varies with wavelength as shown from the IRF test in figure S1. It is inconvenient to comparatively investigate the global relaxation dynamics versus the probe wavelength. Chirp correction is needed to synchronize the signal at different wavelengths.



Figure S2. 3D images of the TA spectra for the three CAS NCs.



Figure S3. Principal kinetics of Cu<sub>3</sub>SbS<sub>4</sub> (a), and Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub> (c)NCs by global time fit. Corresponding principal spectra shown in (b) and (d).

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