One Pot Synthesis and Third-order Nonlinear Optical Properties of $AgInS_2$ Nanocrystals

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Supporting information

The precursor $[(Ph_3P)_2Ag(\mu\text{-}SC\{O\}Ph\text{-}S)_2In(SC\{O\}Ph)_2]$ (MW.= 1296, 0.039 mmol, 50 mg) was added to dodecanethiol (DT, $C_{12}H_{25}SH$, Aldrich, 1.93 mmol, 0.46 ml) and oleic acid (OA, $C_{17}H_{33}COOH$, Aldrich, 1.38 ml) at room temperature (the molar ratio of precursor : DT =1:50; the volume ratio of DT : OA =1:3) and the contents were heated at 200^{o}C for 2 h with gentle stirring under nitrogen atmosphere. The solution was cooled to ~ 70^{o}C and then an excess of ethanol was added, and a flocculent precipitate was formed. The solid was separated by centrifugation, washed with ethanol and dried. This can be easily re-dispersed in non-polar solvent like toluene and hexane.

X-Ray powder diffraction patterns were obtained using a D5005 Bruker X-ray diffractometer equipped with Cu Kα radiation. The accelerating voltage and current were 40 kV and 40 mA respectively. Samples were prepared on glass slides. A concentrated toluene solution was slowly evaporated at room temperature on a glass slide to obtain a sample for analysis. Transmission Electron Microscopy (TEM) was performed on a Philips CM 10 microscope operating at 100 KV. High Resolution Transmission Electron Microscopy (HRTEM) images and electronic diffraction pattern were obtained from a JEOL JSM-3010 instrument. The samples for TEM were prepared by placing one drop of a dilute solution of sample in toluene onto a Cu grid (300 mesh). And then it was completely dried under vacuum. X-Ray photoelectron spectroscopy (XPS) studies X-ray photoelectron spectra were obtained from an ESCALAB MKII spectrometer (VG Scientific) using Al-Kα radiation (1486.71eV). Spectral correction was based on the graphite C1s level at 284.5 eV. The vendor-supplied XPSPEAK version 4.1 was used to deconvolute the XPS data, using fixed half widths and fixed spin orbit splitting in first trials.

$$\left|\chi_r^{(3)}\right| = \sqrt{\left(\mathrm{Im}\,\chi^{(3)}\right)^2 + \left(\mathrm{Re}\,\chi^{(3)}\right)^2}$$

Equ 1.third-order susceptibility equation

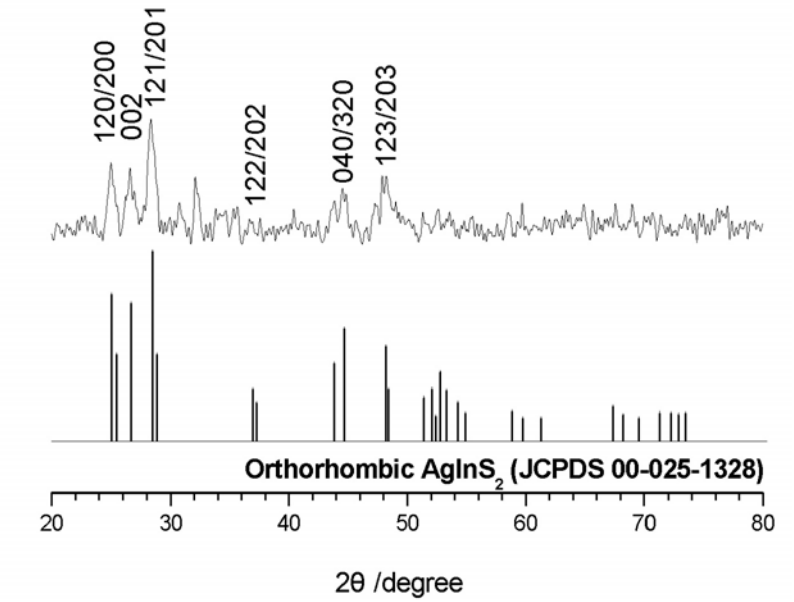

Figure S1. XRPD patterns of the product quenched at 70°C (top) and the simulated diffraction patterns from the JCPDS database (bottom).

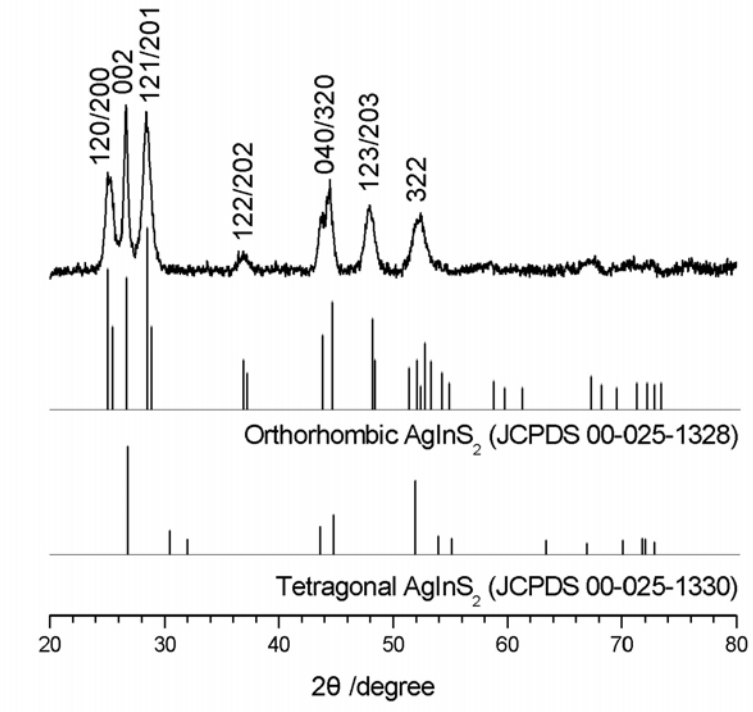

Figure S2. Representative X-ray diffraction patterns of $AgInS_2$ NCs formed at 200 ^oC (top), the simulated diffraction patterns of orthorhombic phase $AgInS_2$ (JCPDS 00-025-1328) (middle) and the simulated diffraction patterns of tetragonal phase $AgInS_2$ (JCPDS 00-025-1330) (bottom).

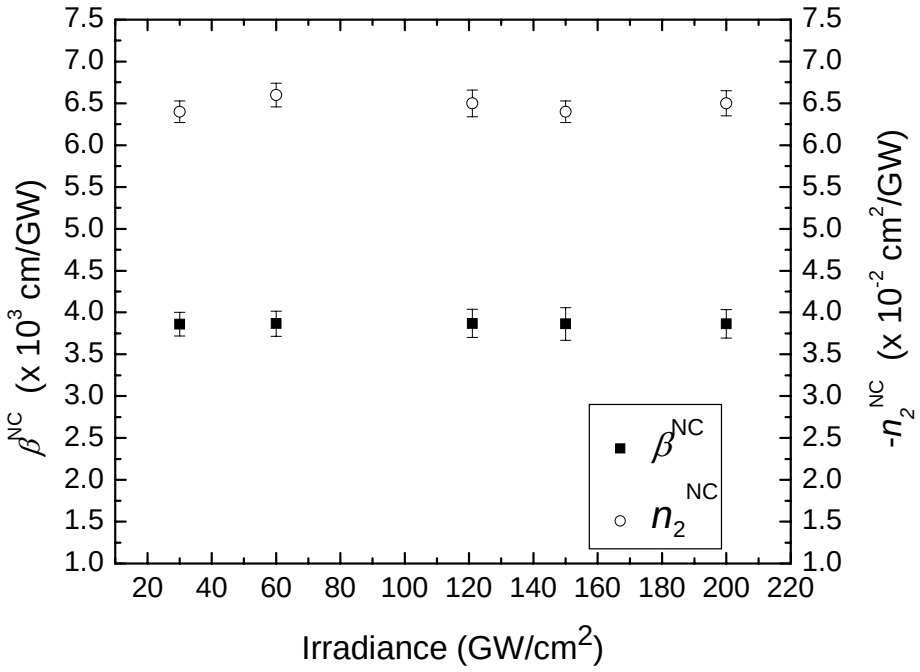

Figure S3. Irradiance independence of the nonlinear absorption coefficient (β^{NC}) and nonlinear refractive index (n_2^{NC}) for the $AgInS_2$ nanoparticles measured at 780 nm.

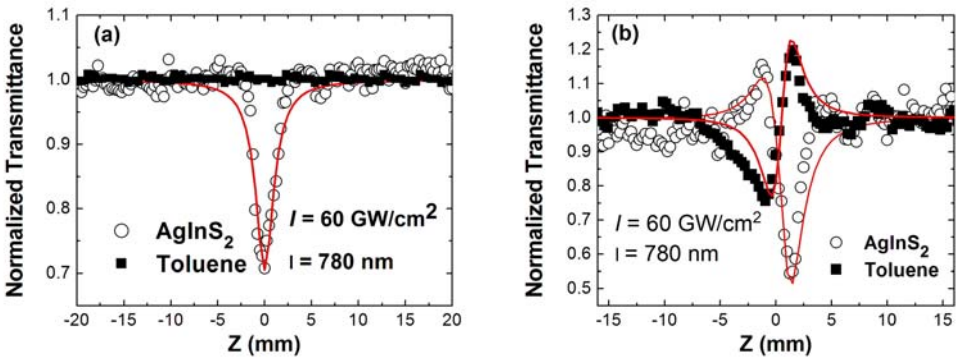

Figure S4. (**a**) Open- and (**b**) closed-aperture Z-scan results of toluene and $AgInS_2$ nanocrystals performed at the same wavelength of 780 nm and irradiance of 60 GW/cm^2. The volume fraction of $AgInS_2$ nanocrystals in toluene is 1.81×10^{-4}.