One Pot Synthesis and Third-order Nonlinear Optical Properties of AgInS₂ Nanocrystals

Lu Tian, Hendry Izaac Elim, Wei Ji and Jagadese J. Vittal

a Department of chemistry, National University of Singapore, 3 Science Drive 3, SINGAPORE 117543. E-mail: chmjjv@nus.edu.sg

b Department of Physics, National University of Singapore, 2 Science Drive 3, SINGAPORE 117543. E-mail: phyjiwei@nus.edu.sg

Supporting information

The precursor [(Ph₃P)₂Ag(μ-SC{O}Ph-S)₂In(SC{O}Ph)₂] (MW. = 1296, 0.039 mmol, 50 mg) was added to dodecanethiol (DT, C₁₂H₂₅SH, Aldrich, 1.93 mmol, 0.46 ml) and oleic acid (OA, C₁₇H₃₃COOH, 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°C for 2 h with gentle stirring under nitrogen atmosphere. The solution was cooled to ~ 70°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.
\[ |\chi_r^{(3)}| = \sqrt{(\text{Im} \chi^{(3)})^2 + (\text{Re} \chi^{(3)})^2} \]

Equation 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 °C (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 ($\beta^{NC}$) 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 $1.81 \times 10^{-4}$. 