

Supplemental Information

Materials: Toluene (99.5%), and isopropyl alcohol were received from VWR International. 1-dodecanethiol (DDT) (98%) and hexanoic acid (98%), were received from Alfa Aesar. Oleic acid was received from Merck. Octadecene (90%), and gallium(III) acetylacetonate (99.99%) were received from Sigma-Aldrich. Silver nitrate and sulfur were received from Fisher Scientific. Methanol (99.99%) was received from PHARMCO-AAPER.

Methods:

Standard AgGaS₂ Synthesis: Syntheses were done on a Schlenk line and with magnetic stirring. Silver nitrate (.2 mmol), gallium(III) acetylacetonate (.2 mmol), and hexanoic acid (.8 mmol), were measured into a 25 mL 3-neck round bottom flask with 5 mL of octadecene as solvent. Solutions were degassed for 30 minutes then heated to 170°C. The reaction was switched to nitrogen gas at 70 °C-80 °C. Upon reaching 170 °C a fast injection of elemental sulfur (.8 mmol) in 5 mL of 1-dodecanethiol was performed. After 45 minutes at 170 °C the temperature was increased to 240 °C for growth and annealing for approximately one hour. Nanocrystals were cleaned by precipitation and centrifugation using isopropyl alcohol and methanol as anti-solvents followed by re-suspension in toluene.

Reaction Sampling: In order to sample the reaction at various times during growth, aliquots were taken directly from the reaction vessel and rapidly diluted in toluene to stop growth. Fluorescence measurements were taken directly of these dilute aliquots. The aliquots were cleaned by precipitation and centrifugation as described above before analysis by TEM or EDS.

Transmission Electron Microscopy (TEM): TEM imaging was performed at Roanoke College on a Philips CM20, 200kV transmission electron microscope with a tungsten filament and equipped with a 3-megapixel AMT bottom mount CCD camera. All samples were prepared on 3mm carbon coated grids from dilute solutions.

Energy-Dispersive Spectroscopy (EDS): EDS was performed on a JEOL 2100 TEM at Virginia Tech's Nanoscale Characterization and Fabrication Lab (NCFL) in coordination with the Virginia Tech National Center for Earth and Environmental Nanotechnology Infrastructure (NanoEarth). The instrument was equipped with a JEOL JED-2200 silicon drift detector with a 60 mm² active area. For each reaction time reported in the communication approximately 7 – 10 locations were analyzed for a given aliquot.

X-Ray Diffraction: X-ray diffraction was performed on a Rigaku Miniflex II benchtop diffractometer equipped with a pulse height analyzer (PHA), and operated at 30 kV and 15 mA with a Cu source. The samples were mounted on zero-background holders made of silicon cut parallel to (510). Most scans were made with steps of 0.05 degrees 2 theta and integrated over 10 s per step.

Fluorescence: Fluorescence was monitored using an Ocean Optics QE Pro with a back thinned, cooled CCD array with a range of 350 nm – 1100 nm, and controlled using Ocean Optic's OceanView software package. The excitation source was a Thorlabs M405F1 fiber coupled 405 nm LED. Samples were measured in a quartz cuvette held in a Thorlabs CVH100 sample holder with a 90° collection angle.

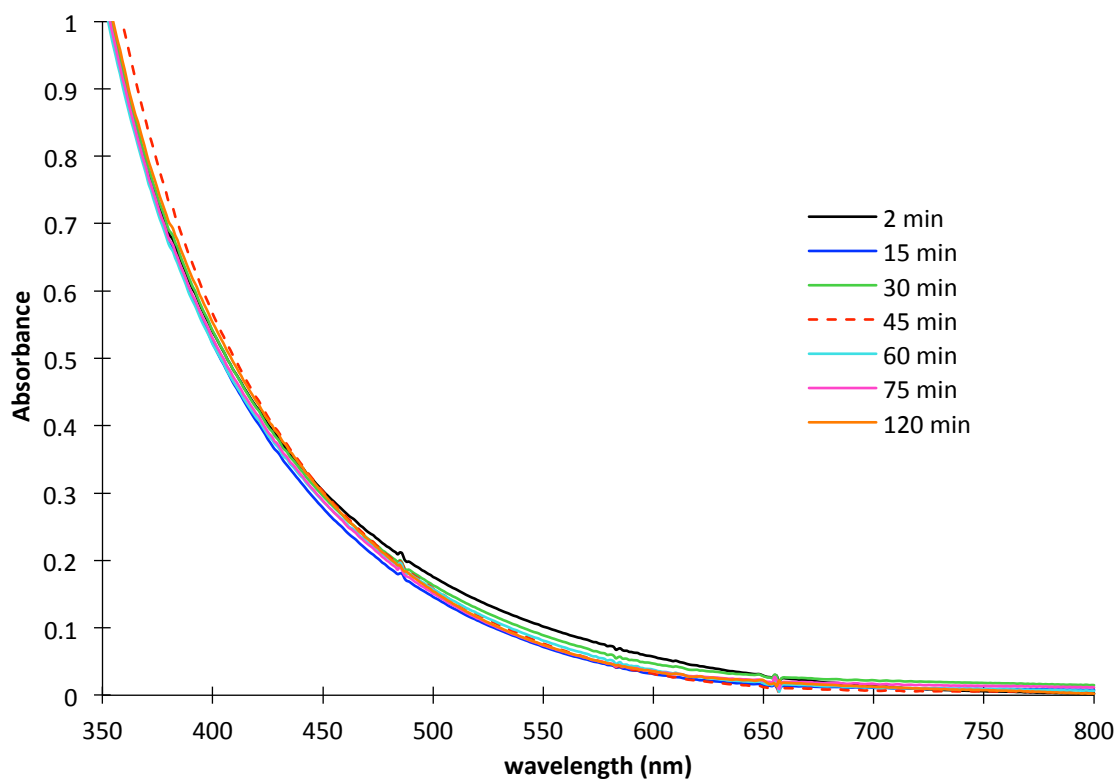


Figure S1. Baseline corrected UV-Vis absorption spectra for samples shown in Figure 1 and S2.

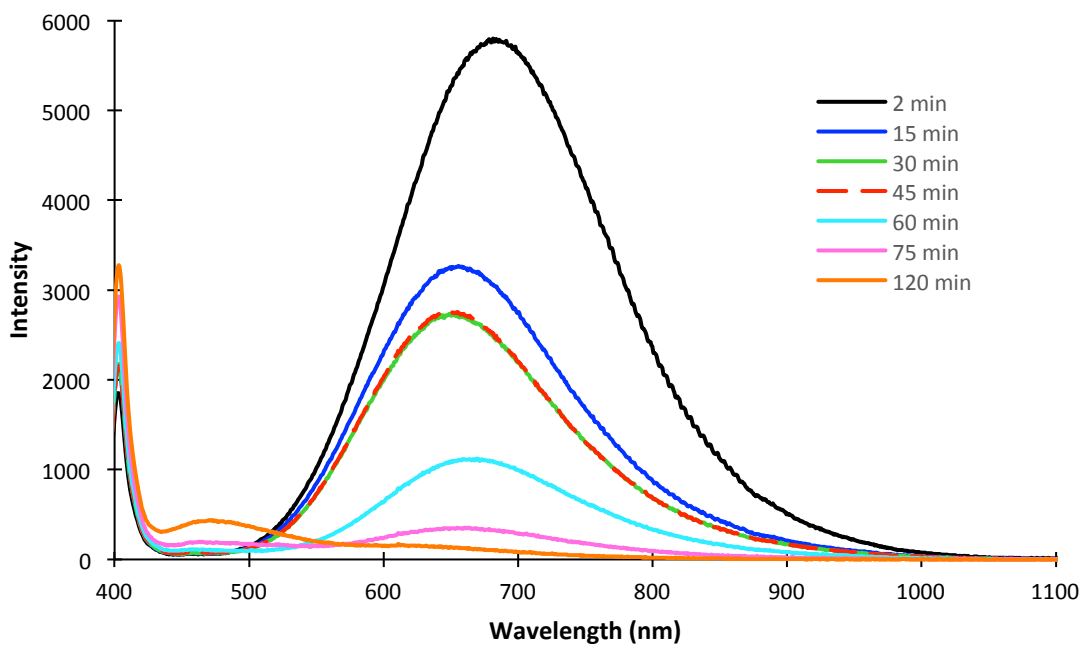


Figure S2. Complete fluorescence spectra for sample shown in Figure 1. Peak at 405 nm is the excitation source.

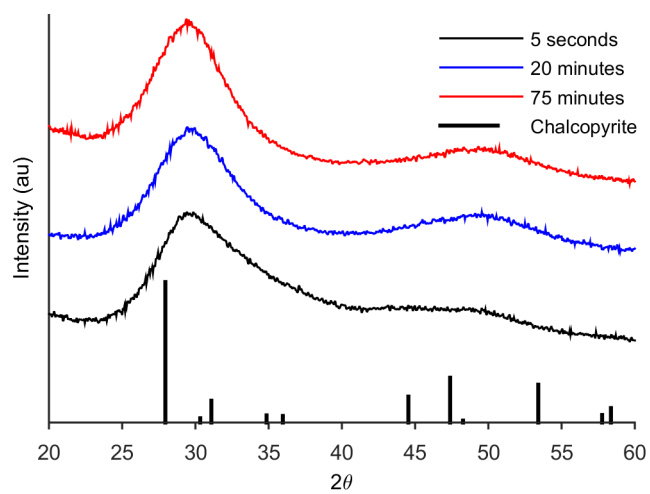


Figure S3. XRD progression shown with reference pattern for chalcopyrite (tetragonal) AGS.