# Supporting information: plasma synthesis of stoichiometric $Cu_2S$ nanocrystals stabilized by oleylamine

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## Experimental details

$Cu_2S$ nanocrystals were synthesized in a flow-through nonthermal plasma reactor shown schematically in Figure 1. The plasma reactor system was comprised of precursor bubblers and a plasma tube sealed between two ultra-torr fittings and pumped using a rotary vane pump. The precursors were elemental sulfur (Sigma-Aldrich, Saint Louis MO) and hexafluoroacetylacetonate Cu(I) vinyltrimethyl silane ((HFAC)Cu(VTMS), 90%, Gelest, Morrisville PA). Solid sulfur was placed in a stainless steel cylindrical enclosure (2 cm inner diameter, 3 cm height), which hereafter is referred to as the bubbler. The bubbler containing the sulfur was heated to and maintained at 125 °C, above the melting point of sulfur. Argon was passed over the surface of the liquid sulfur instead of bubbling through it, to prevent clogging of the gas feed lines. The argon-sulfur mixture was fed to the plasma reactor through a heated gas line maintained at 150 °C to avoid sulfur condensation. The plasma reactor was not heated externally. The (HFAC)Cu(VTMS) was fed from a bubbler maintained at 51 °C also using argon as the carrier gas. The gas lines connecting the (HFAC)Cu(VTMS) bubbler to the plasma reactor were heated to 100 °C to prevent condensation of (HFAC)Cu(VTMS). A third argon stream was also fed into the plasma and served both to control the residence time and to dilute the precursors. The 2.54 cm outer diameter and 1.91 cm inner diameter discharge tube was made of fused silica. The length of the reaction zone (the plasma) was 13 cm. The pressure in the discharge tube during synthesis was 266 Pa (2 Torr). The pressure was monitored by a capacitance manometer pressure gauge (Edwards Barocel 655, 10 torr FSR) and controlled using a valve in front of the rotary vane vacuum pump. A ring-shaped electrode was wrapped around the discharge tube midway between the upstream and downstream ultra-torr fittings. The downstream vacuum fitting served as the ground electrode. The plasma was generated by applying radiofrequency (RF) power, at a frequency of 13.56 MHz, between the ring and the ground through a custom impedance matching network. The nominal power dissipated in the plasma was 80 W, as measured from the display of the RF power supply. The light emission from the plasma was monitored using an optical fiber aligned with the cylindrical axis of the discharge tube. With this arrangement, the emission intensity is integrated over the entire length of the plasma. Optical emission from the plasma, collected by the optical fiber, was dispersed and detected using a spectrometer equipped with a diode array detector (SD2000, Ocean Optics). The relative concentrations of various plasma species were monitored using actinometry. Nanocrystals were collected on an $SiO_2$ filter (Tissue Quartz, Pall Corporation, Ann Arbor MI) placed downstream of the plasma. Nanocrystal collection was monitored using the rise in the reactor pressure as an indicator: the reactor pressure rises slowly as nanocrystals build a cake on the filter. The pressure rise was compensated for by adjusting the throttle position of the valve in front of the vacuum pump, until the filter was completely clogged and the production was stopped. Typical collection times until this happened were a few minutes. If the precursors were fed into the reaction tube with no plasma, there was an insignificant pressure rise over 5 minutes, indicating that an insignificant amount of nanocrystals was produced.

The $Cu_2S$ nanocrystals were extracted from the reactor by first venting with argon to bring the pressure up to atmospheric pressure over the course of approximately 10 seconds. The filter was then extracted from the reactor and sectioned in the laboratory ambient into three pieces, each containing approximately 10 mg of nanocrystals. One section was immediately placed into a pre-prepared solution of 0.09 M oleylamine (OAm) dissolved in toluene. This mixture was sonicated for 30 minutes at room temperature to disperse the nanocrystals in toluene. During sonication, the integrity of the $SiO_2$ fiber filter was compromised resulting in large filter fragments floating around in the solution. The large fragments resulting from the breakup of the filter during sonication were removed by centrifugation at a speed of 4000 RPM. The final result was a clear brownish dispersion. One of the three sections of the filter was left exposed to air in a vial on the bench top for 2 months. After two months, the air-exposed crystals were capped with oleylamine and dispersed using the same procedure for ultraviolet-visible-near infrared (UV-VIS-NIR) absorption measurements.

Samples for powder X-ray diffraction (XRD) and compositional analysis by x-ray energy dispersion spectroscopy (X-EDS) were prepared by pressing a silicon (for XRD) or aluminum foil (for X-EDS) substrate onto the filter-supported nanocrystal powder. XRD from the nanocrystals transferred onto the silicon substrate was collected using an area detector in a Bruker D8 Discover diffractometer that employed Cu Kα radiation. The composition of the nanocrystals transferred onto the aluminum foil was examined using X-EDS in a JEOL 6700 scanning electron microscope at an accelerating voltage of 15 keV.

Transmission electron microscopy was carried out in an FEI Tecnai T12 operating at 120 kV. The specimen support was a copper grid with a holy carbon network that had an ultrathin (~3 nm) continuous carbon film (Ted Pella). Particles were imaged through the ultrathin carbon film, away from the holey carbon support. The particles were deposited on the TEM specimen supports in two different ways. For the particles with no OAm capping agent, the grid was carefully pressed onto the powder accumulated on the collection filter (Figure 1). For the OAm-capped particles, the collection filter was immediately placed into a few milliliters of OAm-toluene solution (see above) and sonicated for 10 minutes. Large filter fragments were removed using a tweezers and then centrifugation. The OAm-capped particles were washed to remove excess ligand by the following procedure. Excess methanol was added to the OAm-toluene-$Cu_2S$ NC solution, which causes aggregation. After aggregation, the solution was centrifuged to separate the particles as a sediment at the bottom of the vile. The supernatant was removed, leaving behind the nanocrystals. The nanocrystals were then dispersed in hexane and the washing procedure was repeated. Finally, the clean nanocrystals were placed on the specimen support and imaged by TEM.

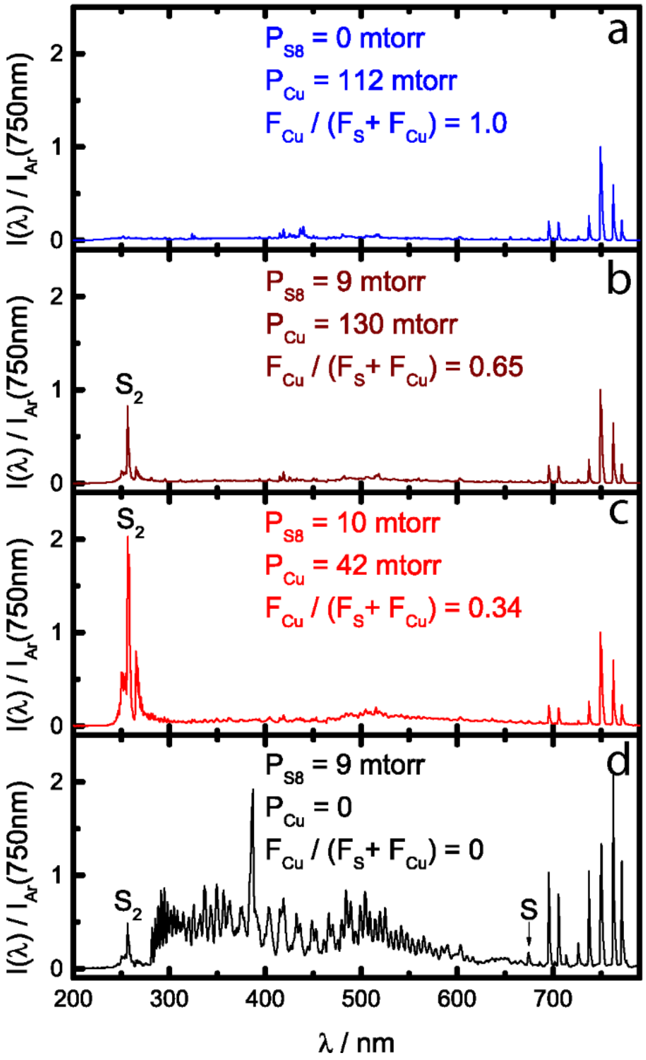

**Figure S1:** Optical emission spectra of the plasma with different molar feeds rates of elemental sulfur and (HFAC)Cu(VTMS) ($F_{Cu}$ and $F_S$ where $F_S = 8*F_{S8}$). The intensities were normalized by the Ar I emission at 750 nm.

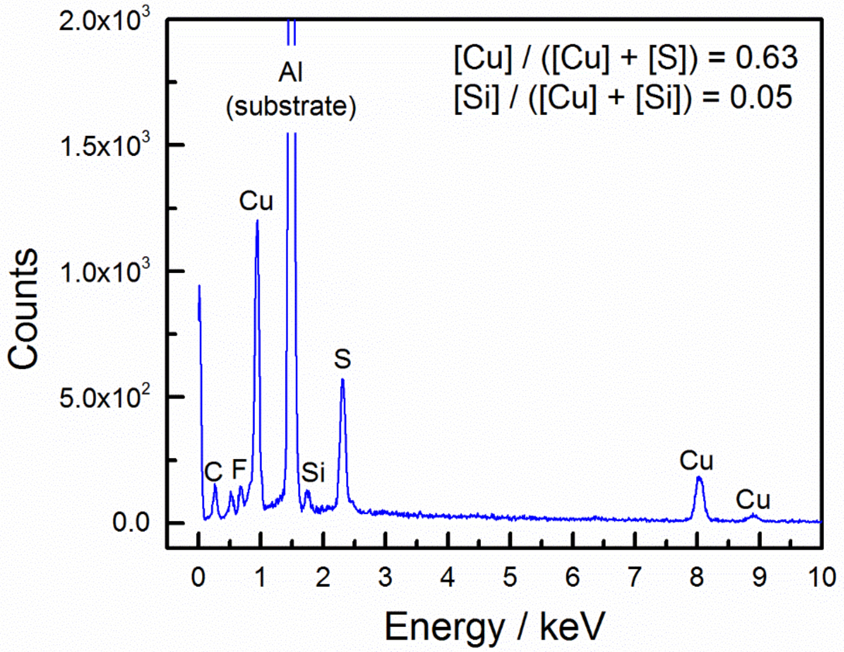

**Figure S2.** X-EDS spectrum of the $Cu_2S$ nanocrystals under illumination by a 15 keV electron beam. The Si content was approximately 5% based on copper, but it should be noted that this value is near the lower limit where quantification becomes unreliable.

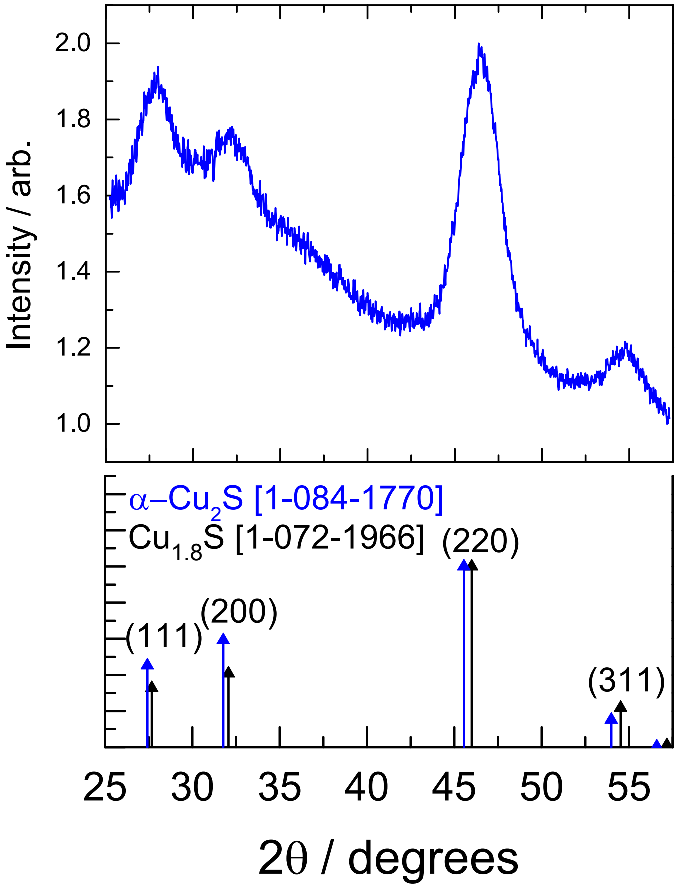

**Figure S3.** XRD pattern of the as-produced $Cu_2S$ nanocrystals (top) and matching PDF patterns (bottom). The average crystallite size measured from the peak broadening using the Scherrer equation was 3.5 nm.

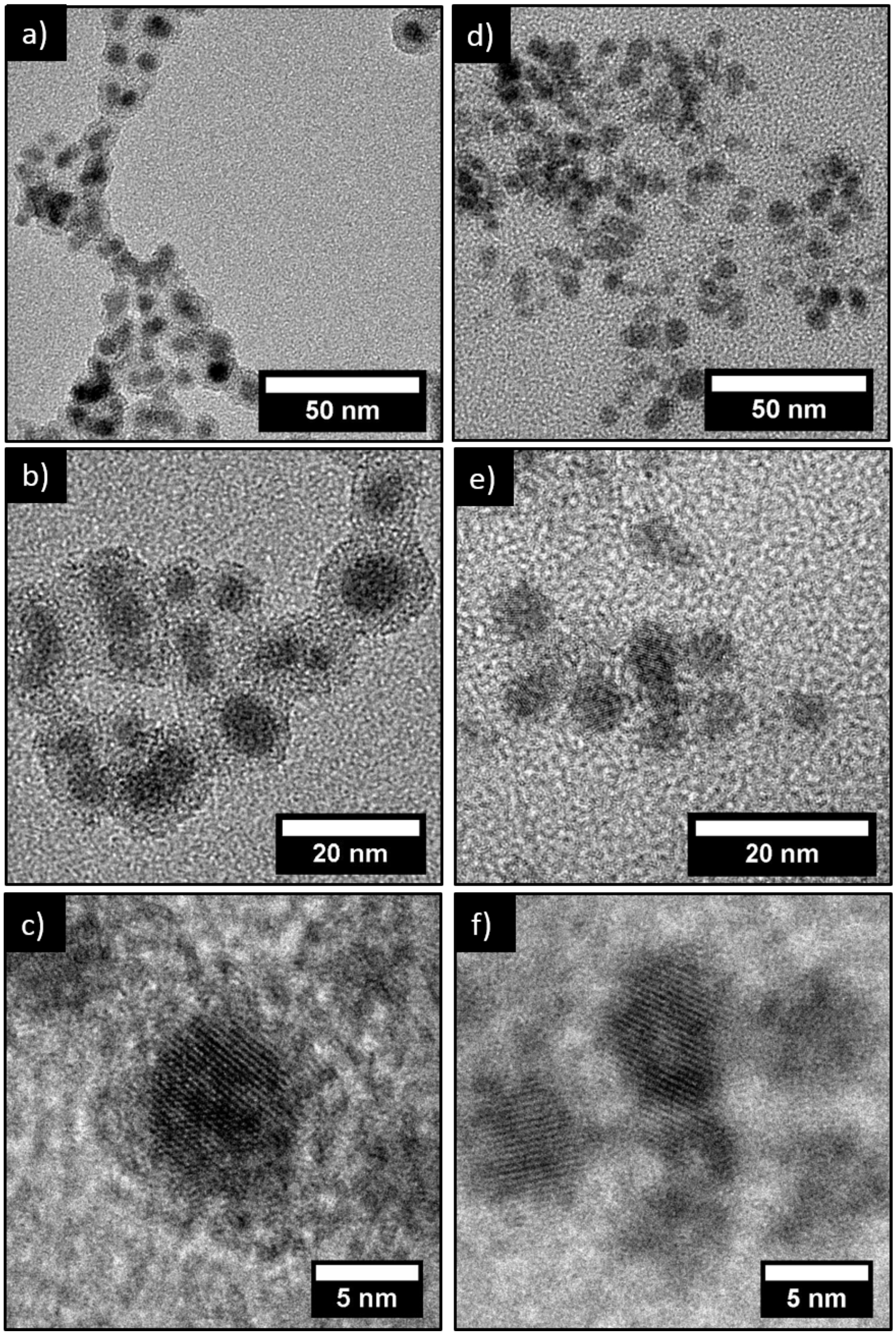

**Figure S4.** TEM images of $Cu_2S$ particles after one hour of air exposure at room temperature, (a-c) without, and (d-f) with, OAm capping immediately after plasma synthesis. An oxide shell, approximately 4 nm in thickness, is clearly visible in panels (a) and (b) that is absent in panels (d) and (e), because the OAm capping agent has suppressed oxidation in (d-f). The core of the oxidized particles is crystalline, which can be seen in panel c). The particles in panel f) are also crystalline, and lattice fringes are visible.