Controlled Surface Chemistry for the Directed Attachment of Copper(I) Sulfide Nanocrystals

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Supporting Information

Ever-growing demand on our traditional energy resources makes harnessing underutilized alternative energy sources all the more necessary and desirable to the scientific community. Colloidal copper(I) sulfide nanocrystals (NCs) are an attractive photovoltaic device component due to their solar absorption characteristics. Copper(I) sulfide is a $p$-type semiconductor with a bandgap reported from 1.1 to 1.4 eV, and an absorption coefficient of $10^4$ cm$^{-1}$. Copper(I) sulfide is also a parent material to ternary and quaternary copper sulfides such as CuInS$_2$, which has emissive defects that can be used for LED lighting, biomedical applications and solar concentrating.

The light-absorbing characteristics of copper(I) sulfide can be further enhanced by morphologies that increase the absorption cross section of the nanocrystals. Manipulating reaction mixture additives can generate highly faceted Cu$_2$S nanocrystals, and careful stabilizer control has been used previously to maintain Cu$_2$S nanoribbons from nanocrystal assemblies in aqueous media. Sadler et al. were first to synthesize Cu$_2$S nanorods through cation exchange with CdS nanorods, a process that lacks atom economy and generates a cadmium byproduct. Additionally, the cation exchange process likely leaves the Cu$_2$S doped with Cd ions. Kruszynska et al. discovered that substoichiometric Cu$_{2-\delta}$S nanorods could be grown from nucleations when using tert-DDT as a ligand and sulfur source, but the fully stoichiometric Cu$_2$S was not achieved. Further developments to prepare rods structures without cadmium and of controlled stoichiometry are needed.

The oriented attachment of Cu$_2$S seed particles into larger single crystalline structures offers a means to obtain nanostructures with morphologies, sizes and compositions that may not be possible with traditional monomer-based growth. Oriented attachment of PbSe performed by Cho and later by Koh produced nanowires, nanorings, and nanorods from single-particle building blocks. Oriented attachment has also been used to create single-crystalline chains of TiO$_2$ crystals, CdTe nanowires, and nanorods of ZnO, CdS and Ag$_2$S. The process occurs due to dipole interactions between particles. Hexagonal-like crystal structures (as shown in ZnO, CdS and Ag$_2$S) inherently have a dipole due to crystal structure anisotropy, yet control over the surface chemistry was essential to orchestrate the directed attachment in many of these cases. The room temperature crystal structure of stoichiometric Cu$_2$S (low chalcocite) and substoichiometric crystal structure djurleite (Cu$_{1.96}$S) consist of copper atoms arranged around a distorted hexagonally close-packed sulfur sublattice (approximated here for simplicity by the hexagonal high chalcocite structure). Provided the surface chemistry can be effectively controlled, this structural anisotropy leaves the door open for the oriented attachment of Cu$_2$S.

Our group’s research has shown that Cu$_2$S nanocrystals synthesized with alkanethiols acting as both the ligands and sulfur sources result in the ligand alkanethiolate sulfur atoms becoming integrated into the crystal lattice. These “crystal-bound” thiolate ligands have sulfur atoms that sit in high-coordination-number sites, and are resistant to ligand exchange and photooxidative disulfide formation. Robust ligand binding in Cu$_2$S nanocrystals has enabled the selective cleavage of ligands at higher temperatures and deposition of metal on exposed edge sites, resulting in nanoscale inorganic cages. Higher synthesis temperatures result in cleavage of the surface ligands through a breaking of the C=O bond. The Kolny-Olesiak group observed that rods could be grown in the direction of crystallographic anisotropy (corresponding to the c-axis of chalcocite) using t-DDT as the sulfur source, suggesting that the c-facet can be selectively activated. This highly defined surface chemistry where ligands are not labile and are cleaved at specific temperatures, is an opportunity to develop oriented attachment-based syntheses for Cu$_2$S.

Here we present a new synthetic route to Cu$_2$S nanorods in which copper sulfide NCs with crystal-bound ligands are joined through the mechanism of oriented attachment in the presence of 1,2-hexanediol (HDD) (Figure S1). Often shown in nanocrystal literature as a reducing agent, evidence discussed herein suggests that HDD functions as a nanocrystal stabilizer necessary to the oriented attachment process. It was found that control of the concentration of HDD was critical to successful directed attachment of nanocrystals in nanorod syntheses, and that the nanorod product had surface chemistry and a crystal structure similar to the constituent NCs.

Prior to the nanorod synthesis, monodisperse quasi-spherical seed nanocrystals with crystal-bound thiol ligands were prepared using a modified literature synthesis. Briefly, Cu(acac)$_2$, 1-dodecanethiol (DDT) and dioctyl ether (DOE) were heated under inert atmosphere to 215 °C for 1 h. The 12–14 nm seeds were then transferred into a glovebox and purified. For the nanorod synthesis, ~$3.7 \times 10^{14}$ NCs were then heated in 3 mL of DOE with HDD (50 mg, 193 μmol) for 1 h and subsequently washed with polar solvents to remove unreacted precursors. The seed NCs had a native crystal-bound DDT surface density of 3.7 molecules/nm$^2$ as
determined by thermogravimetric analysis; 50 mg of HDD equates to more than 50 molecules/nm² (Supporting Information contains experimental details and ligand density calculations).

Figure 1A,B shows TEM images of the seed nanocrystals and nanorods that have a diameter of 12.0 ± 1.0 nm and 13.0 ± 1.3 nm, respectively. The rod length distribution at 20 min of reaction time (Figure 1C) has peaks at regular size intervals, which is a hallmark of the oriented attachment mechanism. After 60 min of reaction, the average rod length does not increase, however the distribution loses its regularity due to slight variations in length likely due to ripening. Similarly, the rod diameter increased from 13.2 ± 1.1 to 14.6 ± 1.1 nm from 20 to 60 min. Additionally, the number of rods increases with respect to the number of solitary particles (vide infra). TEM images of underdeveloped rod samples show characteristic “peapod” shapes indicative of oriented attachment (Figures 1D and S2).

Preferential alignment along the chalcocite c-axis is evidenced by FFT of HRTEM of nanocrystals in the process of oriented attachment (Figure S3). The nanorods in Figure 1E (details in Figure S4) show d spacings of 3.4 Å, which correlate to the (002) plane of the high chalcocite crystal structure. Similar to the results of Kruszynska et al., precipitates of nanorod self-assemblies were recovered at the end of the reaction (Figure S5). TEM of the nanorods often show self-assembled three-dimensional structures containing on the order of 10s of nanorods. Because the disparity in rod diameter is already quite small (<10%), in future work, increased monodispersity in the lengths could result in more extended self-assemblies (Figure S6). FFT of the vertically aligned rods shown in Figure 1F reveals the lateral facets are in the {100} family of planes. The use of air-free techniques after the synthesis results in stoichiometric Cu₂S; UV−vis absorption analysis of a nanorod solution shows that the rods are not plasmonic (Figure S7). Furthermore, X-ray diffraction (XRD) of seeds and nanorods confirms that the Cu₂S retains the stoichiometric low chalcocite phase after the synthesis (Figure 2A).

A sufficient seed concentration and a synthesis temperature of 220 °C were necessary for successful oriented attachment along the chalcocite c-axis. Although tuning the length of the nanorods was not a focus in this study, it was observed that lowering the seed concentration by a factor of 5 resulted in dimers and solitary nanocrystals (Figure S8). In the future, this observation suggests that seed concentration could be used to control nanorod length. TGA of the seed particles has shown that organics can detach from the nanocrystal surface at 220 °C (Figure S9). Correspondingly, at reaction temperatures of 180 or 200 °C, no attachment was observed because the ligands remain stable. At 230 °C, some oriented attachment was observed at 15 min, but after 1 h the ripening process and uncontrolled agglomeration had surpassed the organized attachment mechanism resulting in polydisperse nanoparticles. It is likely that 220 °C is needed to cleave selectively the crystal-
bound ligands on the metal-rich high energy c-facets, over the lateral {100} facets.

The presence of HDD was also necessary to foster oriented attachment, but only at a very specific concentration. Reactions in which seed nanocrystals were heated in 3 mL DOE without HDD (Figure 3A) resulted in polydisperse, nebulous particles due to ripening and disordered sintering. When a ratio of 50 molecules/nm² was used, nanorods were formed as shown in Figure 3B. Increasing the concentration of HDD by a factor of 5 resulted in solitary particles that did not change in size (Figure 3C, original seed diameter: 13.0 ± 0.4 nm, post-reaction: 12.8 ± 0.9 nm). The requirement of an excess of HDD, but not too much, suggests that HDD is involved in an equilibrium process with the surface.

The hypothesis that the specific role of HDD is to act as a surface ligand is notable, as it most commonly acts as a reducing agent in nanocrystal syntheses. We found no evidence of the products of HDD oxidation in a gas chromatography analysis of the postreaction mixture (Figure S10) and there was no reduction in the concentration of HDD. ¹H NMR of a nanorod solution shows broad aliphatic CH₃ and CH₂ signatures indicative of long chain aliphatic ligands bound to a surface (Figure S11). The peak broadening results from the slow tumbling rate of the nanorods and only signals from the outermost protons are observed. Because the concentration of free HDD does not change, we concluded that the nanocrystals continue to be capped with crystal-bound dodecanethiol, rather than having undergone extensive ligand exchange to HDD.

XPS analysis was used to study further the changes in the surfaces of the seeds and rods. Figure 2B–E compares XPS spectra of seed nanocrystals with crystal-bound thiol ligands (red trace) and nanorods (black trace), which both have the characteristic narrow crystal-bound spectra; Cu₂S NCs with crystal-bound ligands have notably narrow S 2p signals as there are only Cu₂S “type” sulfurs. There are no low coordination (or surface-bound) thiolates, which have a higher binding energy. After the reaction, the S 2p and Cu 2p peaks narrow by losing low binding energy components. We attribute this change in surface chemistry to a change in faceting from a large portion of {101}- and {001}-like facets exposed in the seeds, to predominantly {100} facets in the rods. A small oxygen 1s peak appears in the nanorod sample and could be due to HDD or a DOE remnant after the nanocrystals were cleaned. The small oxygen XPS peak in comparison to the large carbon signal is further evidence that HDD is not a major component of the nanorod ligand corona. Additional discussion and the quantitative analysis of the high-resolution XPS spectra can be found in Figures S12 and S13.

The sum of these observations lead to the conclusion that at 220 °C, the crystal-bound ligands on the c-facets of the seeds are selectively cleaved through irreversible C=S bond cleavage. Without the presence of another stabilizing ligand, the newly exposed high energy surface catalyzes morphological changes and uncontrolled sintering of the particles. In the presence of HDD, a weak diol ligand, the surface is stabilized, preventing these changes. The binding of HDD is in equilibrium with free HDD in solution, so that when an excess of HDD is used, the equilibrium is shifted to “on” and no oriented attachment can occur due to a strong passivation. When a middle ground is found, dipole interactions between particles enable nearby nanocrystals to push through the less-dense HDD barrier and attach along the high chalcocite c-axis. A temporal study of the nanorod synthesis shown in Figure S14 reveals that rods continuously form over the course of the reaction rather than in one event. The study also suggests that the rods are removed from the pool of available material (in self-assemblies) after oriented attachment, as evidenced by the consistent average nanorod lengths shown at 20, 40 and 60 min of reaction time.

For comparison, oleylamine (OlAm) was substituted for HDD under the same nanorod synthesis conditions. The results of this experiment, shown in Figure 4, show that OlAm binds to the surface of the Cu₂S nanocrystals markedly different than HDD and thus alters their shape through lateral ripening rather than oriented attachment. OlAm has a preference for the c-axis facets of Cu₂S and binds strongly, a fact that can be exploited to make platelet nanocrystals. In this experiment, spherical particles doubled in width perpendicular to the c-axis (12.0 ± 1.0 nm to 24.1 ± 2.4 nm), whereas growth along the c-axis was negligible (final length: 13.1 ± 0.7 nm). Columnar assemblies shown in the TEM images of this sample highlight copper(I) sulfide’s preference for c-axis coordination.

This Communication has discussed the use of HDD as a weakly binding stabilizer and facilitator of Cu₂S nanocrystal oriented attachment. Quasi-spherical Cu₂S nanocrystals with crystal-bound ligands were used to synthesize nanorods of similar but slightly ripened diameters. Evidence for oriented attachment was shown in TEM images of peapod-like nanorods and periodic spikes in the distribution of rod lengths. Varying the concentration of HDD had the effect of preventing disordered attachment, and enabled dipole driven interaction to
connect nanocrystals when the quantity of HDD was optimal. Reactions without HDD resulted in ripening and disorganized attachment, whereas reactions with a high concentration resulted in solitary nanocrystals. XPS of seed nanocrystals and nanorods revealed similar surface chemistry with the nanorods. The fwhm of S 2p and Cu 2p decreased in the rod samples suggesting a homogenization of the nanorod surface states. XRD analysis of the nanorods showed that the low chalcocite crystal structure of the seeds is preserved. To the best of our knowledge, this is the first time colloidal stoichiometric Cu2S nanorods have been synthesized without cation exchange. Moving forward, it is hoped that although oriented attachment can result in polydisperse nanorod lengths, quantum confinement can be achieved with smaller seeds due to rod/seed diameter correlation.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b05080.

Experimental details for the seed and nanorod syntheses, TEM, UV–vis and XPS spectra (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


