# Link Foundation Energy Fellowship Report for Adam Brewer

## *Introduction*

As our population continues to grow, I believe that efficiently harnessing clean, abundant solar energy would be a tremendous boon to society. To that end I have explored copper sulfide colloidal quantum dots (CQDs) as a potential route to efficient solar energy. This system has the potential to simultaneously provide high efficiency and low cost solar power due the combination of abundant[1] copper sulfide's optical properties[2] with quantum dot's solution processability[3]. $Cu_2S$ quantum dots may also be applicable to other technologies beyond solar, such as thermoelectrics[4], photodetectors[5], bioimaging[6], and plasmonic light manipulation[7]. However, because of their small size, we need to better understand what influences the surfaces of different quantum dot systems. In particular my research has focused on studying the ligand shell on $Cu_2S$ quantum dots. Specifically whether it can be changed and, if so, do different ligands passivate, or induce, various trap states, which in turn could alter the electronic properties. I present the first explicit study on the effect of surface treatments on $Cu_2S$ colloidal quantum dots, specifically thiols, amines, pyridine and carboxylic acid ligands, as well as chlorination in $CCl_4$.

## *Results*

I set out to study the impact of different surface treatments on the electrical and optical properties of $Cu_2S$ CQDs. First I sought to identify whether or not QDs treated with different ligands had those ligands adhere to the surface, and subsequently studied how the absorption, photoluminescence, mobility, and carrier concentration were affected, if at all.

I used FTIR to identify optical absorption peaks specific to the different ligand functional groups; I found that $Cu_2S$ QDs treated with octylamine result in some amines adhering to the nanocrystal (NC) surface.

Broader spectrum absorption measurements reveal that the amine treatment induces sub-gap absorption, which in copper sulfide is most frequently attributed to a large number of free carriers causing a localized surface plasmon resonance (LSPR)[7]. LSPR was used to estimate a carrier concentration of $1x10^{21}$ $cm^{-3}$ in $Cu_2S$ amine treated nanocrystals. Also from FTIR I saw no trace of carbon-oxygen, or carbon-nitrogen bonds and concluded that pyridine and carboxylic acid do not readily exchange with the native dodecanethiol ligands, not even after being dispersed in the pure ligand at elevated temperature for 24 hours. Looking at the full absorption spectrum I found that pyridine seems to reduce the overall number of ligands on the surface relative to treatment with oleic acid, because pyridine had the same amount of ligand absorption with a greater amount of $Cu_2S$ absorption. The absorption measurements were corroborated with photoluminescence (PL). The photoluminescence was normalized to the concentration of nanocrystals in solution, and for pyridine or octylamine treatment the PL intensity was reduced compared to dodecanethiol and oleic acid ligands. Photoluminescence is sensitive to the number of defects, which serve as nonradiative recombination centers, and so I deduce that thiols may passivate the $Cu_2S$ nanocrystal surface.

I independently measured the increase in free carriers due to amine treatment of $Cu_2S$ quantum dots through the mobility and conductivity. Transconductance measurements provided the first report of $Cu_2S$ CQD mobility ranging from $10^{-5}$ to greater than $10^{-2}$ $cm^2/Vs$ depending on ligand treatment, which is acceptable for solar power conversion efficiency greater than 10%[3]. Using transconductance to measure the mobility of degenerate semiconductors is itself a novel technique offering a lower-bound on the mobility, with actual mobilities up to about 5 times greater depending on the level of degeneracy. I then used the mobility to calculate carrier concentrations in $Cu_2S$ CQDs without LSPR for the first time ($2x10^{19}$ $holes/cm^3$), and I compared the electrically measured carrier concentration for amine treated samples ($4x10^{20}$ $holes/cm^3$) with the carrier concentration calculated from their plasmon resonance, as previously reported in Nature Materials ($1x10^{21}$ $carriers/cm^3$). The discrepancy suggests that the that the current model for plasmon resonance in $Cu_2S$ quantum dots may be incomplete for QD films, probably because it lacks terms taking into account the size of the quantum dots, coupling between dots, and currently requires assumptions on the dielectric constant and hole effective mass[7].

The results of transconductance of $Cu_2S$ also support the idea that thiols passivate the $Cu_2S$ surface. The addition of amines would be expected to increase the number of electrons in the CQD film, but the transconductance revealed an increase in the number of holes with amine treatment. This suggests that removing thiol ligands with amines added holes, which should only occur if an amine removes a thiol ligand that was passivating a hole trap. I also report the first chlorination of $Cu_2S$ nanocrystals which also induces a strong localized surface plasmon resonance. This effect was analyzed with XPS revealing that the $CCl_4$ solvent or, more probably, a small amount of dissolved chlorine or HCl, left over from the manufacture of $CCl_4$, chlorinates the nanocrystals.

*Significance, impact and future prospects*

Abundant and clean energy will be a vital part of a sustainable future, and large area scalable devices will enable many new applications. My work has revealed interesting changes in the defects and electrical properties of earth abundant, easily processed $Cu_2S$ quantum dots. Insight into $Cu_2S$ QD surface chemistry offers the possibility of controlling the plasmon resonant frequencies using different ligand functional groups, or the reduction in carrier concentration for improved solar efficiency through enhancement of the passivating effects of thiol treatment. This knowledge can be used as a starting point for a deeper analysis of copper sulfide, or applied to other quantum dot systems. Further research could then open the door for $Cu_2S$ as a single platform that could be adapted to a variety of low cost electronics, especially solar photovoltaics.

*Expected publications:*

Surface Modification and Electrical and Optical Properties of $Cu_2S$ Colloidal Quantum Dots – In Preparation

*Discretionary funds:*

Discretionary funds were spent on paying for time on scanning electron microscopes ($47/hr) and X-ray photoelectron spectroscopy ($33/hr) instruments in a shared use facility on campus for determining device morphology and Cl incorporation respectively. Funds were also spent on expenses for travel to speak at the 2011 Fall MRS symposium. 1000 dollars remain for contribution towards typically $1000-$2000 paper publishing costs. The delay in publication after the collection of data is unfortunate but typical.

*How the fellowship made a difference:*

The Link Foundation Energy Fellowship allowed me to pursue research I found interesting to a greater depth than I could have on a federally funded grant, and helped create a new direction of research in my group. The fellowship enabled me to study the field of inorganic semiconductors and quantum dots, which are fields I find more broadly applicable to the solar and electronics community than otherwise might have been available. It is been my honor to use the generosity of the Link foundation to study, learn, and educate on quantum dots, colloidal chemistry, degenerate semiconductors, and copper sulfide. I believe my experience as a Link Fellow will continue to open doors well into the future, and for that I am very grateful.

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