Spring 2020

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Robust and Simple Synthesis of CIS/ZnS Refined for High Luminescence in the Near-IR

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Abstract

To increase the efficiency of solar cells, copper indium disulfide- zinc sulfur nanocrystals need to be grown larger to emit further in the range of silicon's optimal absorption and have a higher photoluminescence quantum yield. Typically, the bigger the quantum dot, the lower the photoluminescence quantum yield, making this aim difficult to achieve. Additionally, many syntheses used for this material include large amounts of toxic precursors that would make industry-level production expensive and potentially harmful to the environment. This paper develops a robust synthesis to be used in a wide range of solvents, including unrefined avocado oil, that decreases the amount of precursors and toxic waste while increasing the photoluminescence quantum yield to between 69-85% at a peak emission of 740-760 nm depending on the solvent used.

1. Introduction

With the effects of climate change becoming more prominent with each passing year,[1-3] society is in dire need of a shift from fossil fuels to renewable energy sources.[4,5] Solar photovoltaic (PV) is one of the most promising forms of renewable energy.[6,7] However, solar PV needs to increase efficiency and become more affordable to compete with fossil fuels.[5,7,8] Semiconducting nanocrystals (NCs) can shift the wavelength of light closer to the 0.9-1.5 eV peak efficiency of silicon solar cells. A theoretical model showing how the optical power efficiency of a solar cell depends on the photoluminescence quantum yield (PLQY) and the peak emission of the NCs is shown in Figure 1. Additionally, NCs can be put into a luminescent solar concentrator (LSC) to decrease the surface area of solar cells needed, decreasing costs.
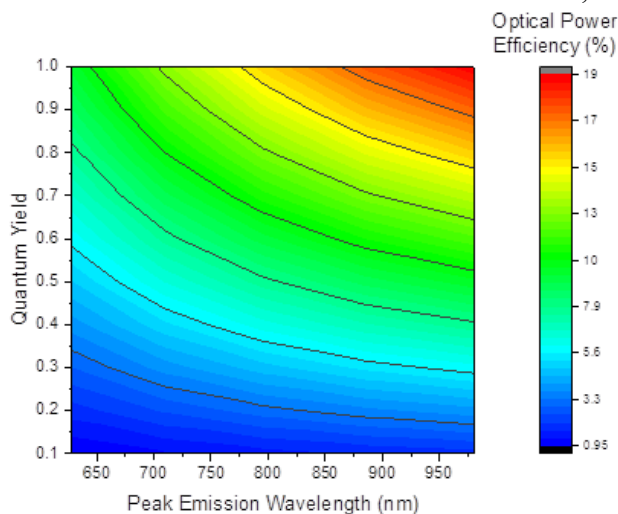

Figure 1. Theoretical optical power efficiency of a solar cell with nanocrystals of a particular photoluminescence quantum yield and peak emission.

One of the more environmentally benign NCs, due to the lack of toxic metals, is copper indium disulfide with a zinc sulfur shell (CIS-ZnS). There are many different syntheses used to create CIS-ZnS, but many of these syntheses would be difficult to scale to industry level due to increasingly green industry standards.[9] New chemical manufacturing methods are expected to be

easy to replicate, be safe for workers, and to produce the least amount of toxic waste possible.[10-13] These requirements are fulfilled by few, if any, currently published syntheses as most rely on toxic solvents such as 1-octadecene (ODE) or oleylamine and use many precursors in excess.[14-17]

A few syntheses utilize non-toxic solvents such as paraffin oil, but the peak emission is too low to optimize silicon solar cell efficiency.[18] Additionally, paraffin oil is a nonrenewable petroleum derivative created during the distilling process.[19] Renewable oils, such as olive oil, have been used in syntheses for both CdS and CdSe NCs.[20,21] In this paper, we compared the use of ODE, paraffin oil, and unrefined avocado oil as solvents in the CIS-ZnS synthesis. Other parameters tested include the ratio of Cu/In, the ratio of Zn/Cu, the temperature of shelling, and the length of shelling.

2 Experimental Methods
2.1 Materials
Copper (I) iodide (99.999%), indium acetate (99.99%), 1-dodecanethiol (DDT, 98%), 1-octadecene (ODE, 90%), Zn stearate (10–12% Zn basis), paraffin oil light medium, hexanes, methanol, ethanol, and isopropanol were purchased from Sigma-Aldrich and used as received. Avocado Oil (California Extra Virgin, Primal Kitchen) was purchased from a grocery store and used as received.
2.2 Development of the recipe
2.2.1 Ratio of copper to indium
Past groups have found that altering the ratio of Cu to In has created different traps in the surface of the nanocrystal core, prompting different emission pathways.[22] To determine which ratio was best for quantum dots emitting at 750 nm, cores were synthesized separately using copper (I) iodide and indium acetate at ratios of 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 mmol Cu/In and 15 mL of DDT. These materials were put in a 250 mL three-necked round bottom flask and stirred using a stir bar while degassed and then flushed with N_2 three times. The vessel was heated to 220°C. Once the core mixture began to shift color, the reaction was allowed to continue until the peak emission was at 820 nm as assessed using the Horiba Fluorolog Fluorometer/Ocean Optics USB Spectrometer. Immediately, the round bottom flask was submerged in a water bath.

To each batch, 8 mmol Zn/Cu was added along with 15 mL paraffin oil and an additional 4.5 mL DDT. This mixture was put under vacuum and flushed with N_2 three times and then heated to 210°C and shelled for 3 hours before being submerged in a water bath. Each batch was purified using precipitation and resuspension in methanol/ethanol, isopropanol, and hexanes in a centrifuge. The collected NCs were resuspended in toluene. The PLQY of each batch was measured using the procedure listed in the PLQY section.

2.2.2 Ratio of zinc to copper
Many recipes use an 8 Zn/Cu mmol ratio, but this excess zinc stearate (ZnSt) makes purification of the final product extremely difficult. To lessen the residual stearate after the shelling step, ratios of 2, 4, 6, 8, and 10 Zn/Cu were used. These batches were produced using a 0.5 Cu/In mmol ratio and the same procedure and purification were used as in 2.2.1. The PLQY for each batch was measured.

2.2.3 Length of shelling at each temperature in paraffin oil
Different syntheses use different temperatures and lengths for coring and shelling.[14-17] The recipe used follows 2.2.1 with a Cu/In ratio of 0.5 and a Zn/Cu ratio of 4. Temperatures of 210, 220, 230, and 240°C were used and every 30 min an aliquot was removed from the synthesis and submerged in a vial of hexanes. PLQY for each time and temperature series were measured.

2.3 Different Solvents
The recipe from 2.2.1 was performed with 0.5 Cu/In, 4 Zn/Cu with different shelling solvents. Paraffin oil, 1-ODE, and avocado oil were used. For each solvent, time to shell at 220°C was retested. Following the purification in 2.2.1, these batches were run through a biobead column to further purify the sample before further testing in TA Instruments Q500 TGA (ramp 10.00 °C/min to 100.00 °C, isothermal for 60.00 min, and ramp 10.00 °C/min to 800.00 °C) and PLQY.

2.4 Photoluminescence Quantum Yield
The PLQY was measured by diluting the purified sample to 0.1 absorbance at 650 nm as measured by a Jasco V-670 UV/Vis. The same sample at 0.1 abs is then excited at 650nm and the emission collected from 650-1000 nm on an Horiba Fluorolog Fluorometer/Ocean Optics USB Spectrometer. The fluorescence intensity of the sample is compared to a standardized dye (HITCI, 28.3%) to calculate the PLQY of each sample .[23]

3. Results and Discussion
3.1 Development of the recipe
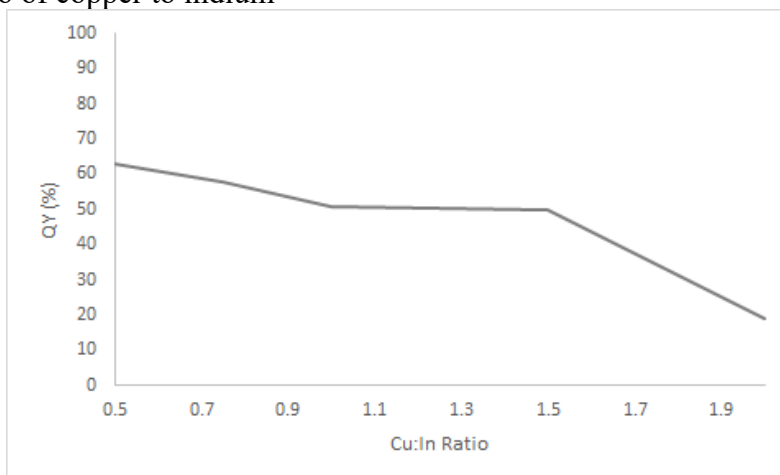3.1.1 Ratio of copper to indium

Figure 2. Photoluminescence quantum yield of different copper to indium ratios.
All batches of varying Cu/In ratios had a peak emission of 750 nm. The batch at 0.25 Cu/In was quenched during synthesis due to the lack of Cu present. However, the next lowest amount of copper, 0.5 Cu/In had the highest PLQY of 63% at 750 nm (Figure 2). Meanwhile, the more indium deficient batches had a much lower PLQY of 20% at 750 nm indicating that the presence of indium with copper defects is important in producing a high photoluminescence quantum yield in the near-IR wavelengths of emission.
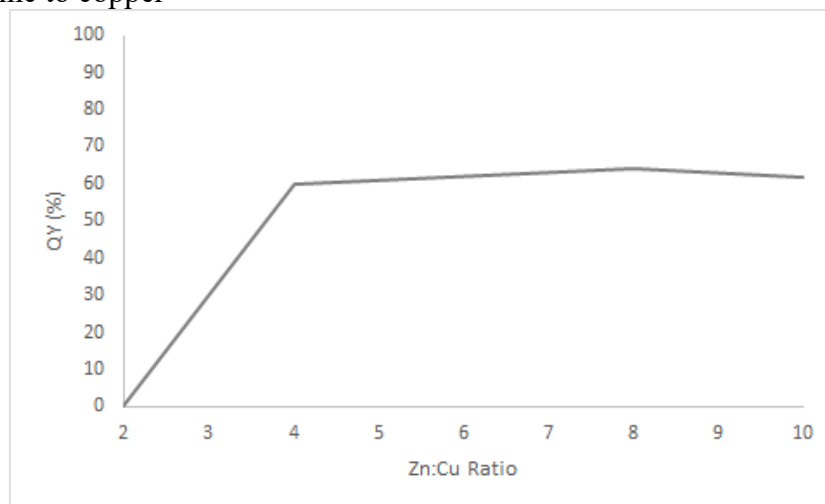
3.1.2 Ratio of zinc to copper

Figure 3. Photoluminescence quantum yield in batches with varying amounts of zinc.

To test if the extreme amount of zinc stearate used in most recipes was necessary to form a shell around the CuInS2 core, the amount of zinc precursors was varied based on a molar ratio of Zn/Cu. A Zn/Cu ratio of 2 is not enough to push forward the formation of a ZnS shell, while 4 Zn/Cu resulted in a PLQY of 60% (Figure 3). The increases in PLQY in the 6, 8, and 10 Zn/Cu batches did not lead to any significant increase in PLQY showing that this excess was unneeded.

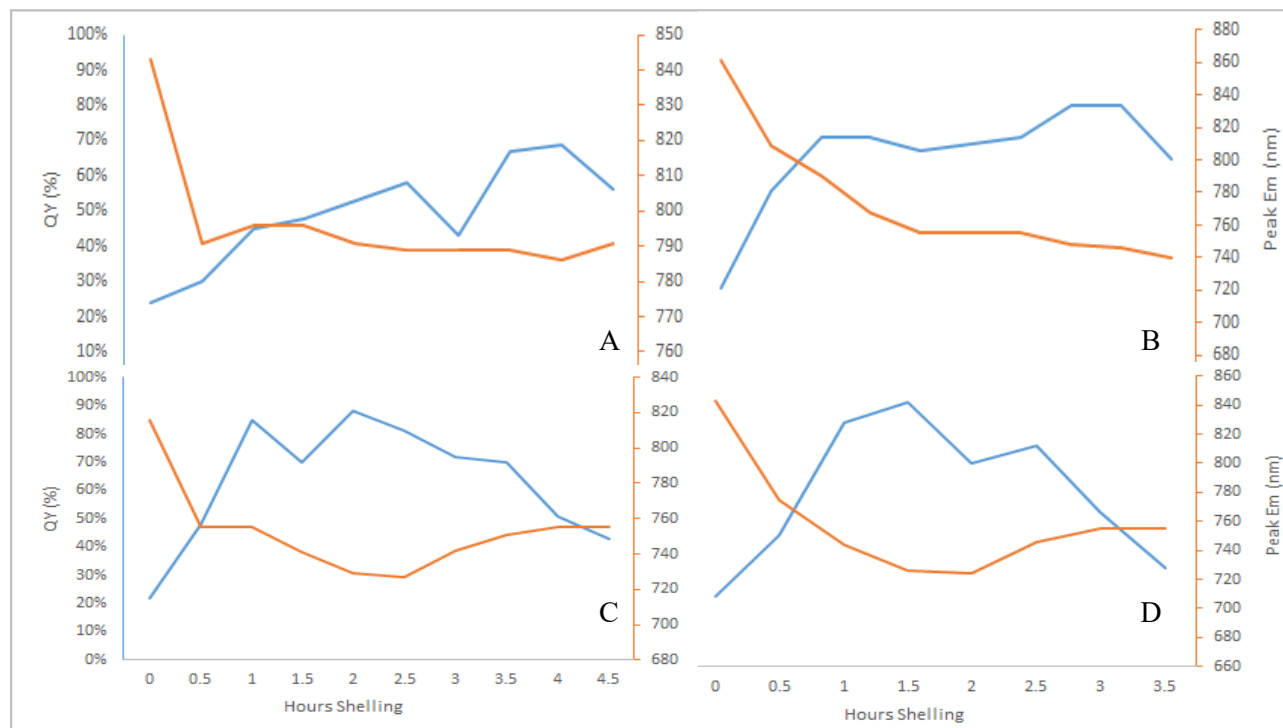### 3.1.3 Length of shelling at each temperature in paraffin oil

Figure 4. Photoluminescence quantum yield and peak emission after various lengths of time in the shelling step. A was performed at 210°C. B was performed at 220°C. C was performed at 230°C. D was performed at 240°C. The orange line represents the peak emission in nm (to the right of each respective graph) and the blue line represents the photoluminescence quantum yield (to the far left of figure).

To determine the optimal temperature for synthesis, four reactions were run at temperatures of 210, 220, 230, and 240°C with samples removed every 0.5 hour for PLQY and peak emission measurements. In graph A of Figure 4, the PLQY increases to 70% after 4 hours with a peak emission of 730 nm when the shelling is performed at 210°C. Meanwhile, a PLQY of 70% at 760 nm was reached in just 1 hour at 220°C and at 3 hours the PLQY had increased to 80% at 750 nm (Figure 4B). At both 230°C and 240°C the quantum dots reached a PLQY of 80% in 1 hour with a peak emission of 750 and 740 nm, respectively (Figure 4C, 4D). However, the fluctuation in peak emission, which is related to the size of the quantum dot, overtime shows that the quantum dots produced at these temperatures are composed of NCs of wildly varying sizes. Meanwhile, the sample at 220°C was able to push the reaction forward faster and produced a more uniform batch of quantum dots as indicated by the peak emission consistently decreasing over time.

3.2 Different Solvents

To determine the effect of the non-coordinating solvent on the synthesis; paraffin oil, avocado oil, and 1-ODE were tested. Figure 3B shows that in paraffin oil the quantum dots were able to reach a PLQY of 78% at 750 nm after 3 hours.
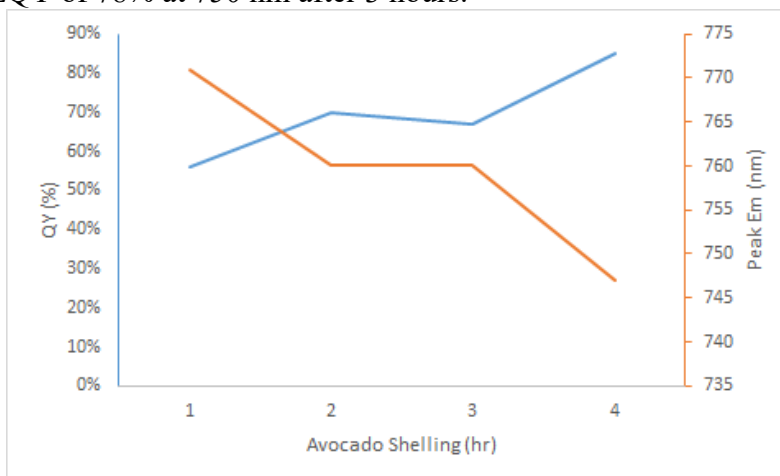

Figure 5. Shelling in avocado oil at 220°C. The orange line shows the peak emission of the batch in nm and the blue line shows the PLQY of the batch.

In unrefined avocado oil, the PLQY reached 69% at 760 nm after 2 hours (Figure 5), which demonstrates that the recipe is highly robust and stable proving that laboratory grade solvents are not required to obtain quality NCs. If a refined avocado oil had been used, then the results may have been more successful.
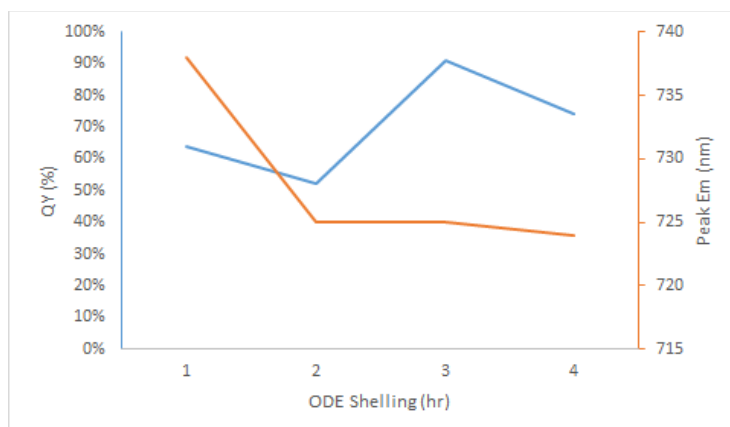
Figure 6. Shelling in 1-ODE at 220°C. The orange line shows the peak emission of the batch in nm and the blue line shows the PLQY of the batch.

In 1-ODE, the PLQY reached 85% at 730 nm after 3 hours (Figure 6). This peak emission is 20-30nm less than those of the other solvents, but the PLQY is around 10% higher. However, during purification, both the batch in paraffin oil and avocado oil were purified after only one round of precipitation/resuspension and biobeading whereas the 1-ODE needed 3 rounds to be comparatively pure. This level of purification is demonstrated in the TGA spectrum (Figure 7).

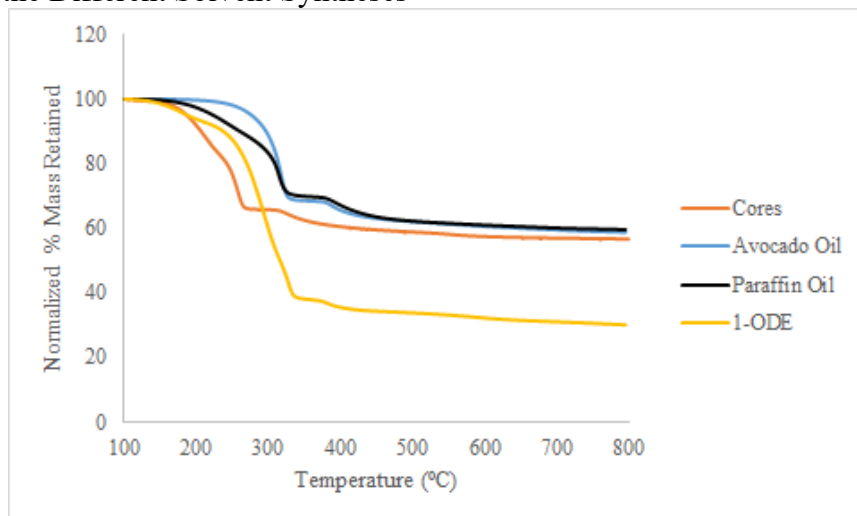## 3.2 TGA from the Different Solvent Syntheses

Figure 7. TGA of CIS/ZnS when synthesized in different solvents. TGA data were analyzed by dividing all data points by the initial mass in each sample.

The first mass loss event at 300°C corresponds to the loss of unbound DDT. The CIS/ZnS synthesized in 1-ODE have significant unbound DDT loss as do the cores. The sample in paraffin oil has some unbound DDT loss and the avocado oil has undetectable amounts of unbound DDT loss (Figure 7). The second mass loss event around 250-325°C corresponds to the loss of bound DDT. Therefore, around 40% of the mass of CIS/ZnS in 1-ODE was bound DDT

while around 35% of the mass was bound DDT in the avocado oil. In paraffin oil, only 20% of the initial mass was bound DDT.

4. Conclusion

The need to improve the efficiency and lower the costs of solar cells can be achieved through the application of CIS/ZnS. However, to produce this material at the scale needed, more work needs to be done to make the synthesis as efficient while minimizing the use and resulting production of toxic materials. In this paper, we were able to determine which ingredients were essential to CIS/ZnS formation and how to reduce the amount of zinc stearate and the solvent significantly while increasing the PLQY and peak emission to a more optimal range by adjusting the ratio of Cu/In and optimizing the temperature and length of shelling. In addition, we were able to show that this recipe can be performed in several solvents as shown in Table 1.

Table 1. Properties of the solvents used and the optical properties of the CIS/ZnS produced.

Solvent	Properties	PLQY (%)	Peak Emission (nm)
1-ODE	Toxic	85	730
Paraffin Oil	Non-toxic, Petroleum byproduct	78	750
Avocado Oil	Non-toxic, Renewable	69	760

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