Synthesis and Characterisation of p-type and n-type CuInS2 Nanocrystals

1 Introduction – What are nanocrystals and their uses?

Nanocrystals (NC's) are semiconducting material particles with at least one dimension smaller than 100 nanometres 1 x10^{-7}m. They are based on quantum dots (QD's), otherwise known as nanoparticles and are composed of atoms in a single- or poly-crystalline arrangement [1].

During the manufacturing of NC's, a trace chemical called a doping agent can be incorporated into the crystals to give them different electrical properties in comparison to pure semiconductor crystals. Two different kind of NC's can be produced;

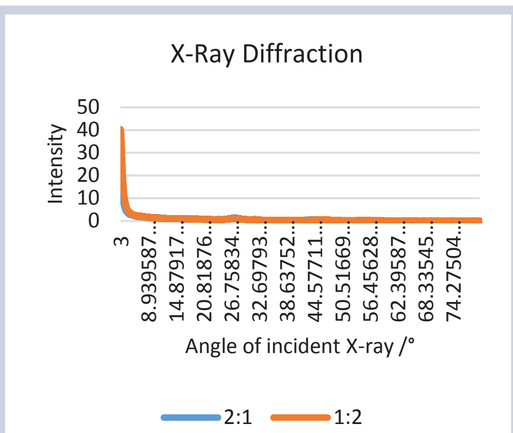
- n-type where the majority of charge carriers are negative electrons
- p-type where the majority of charge carriers are holes, which acts as a positively charged particle

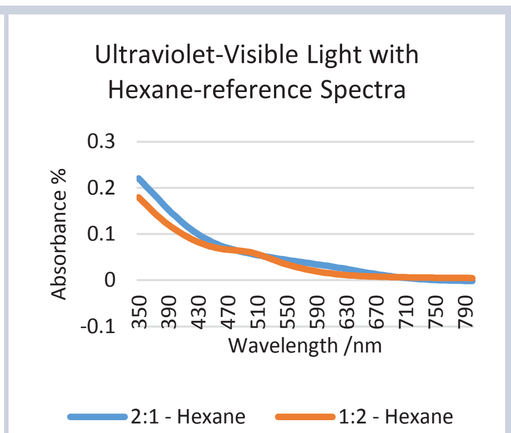
CuInS2 NC's have a promising future in uses of photovoltaic cell absorption materials due to, excellent optical properties; relatively low toxicity; both n-type and p-type NC's can be formed by varying the Cu:In ratio during the synthesis of the crystals and the field of applications is extremely diverse. Perfecting the manufacture of NC's has the potential to advance technology on an unprecedented scale.

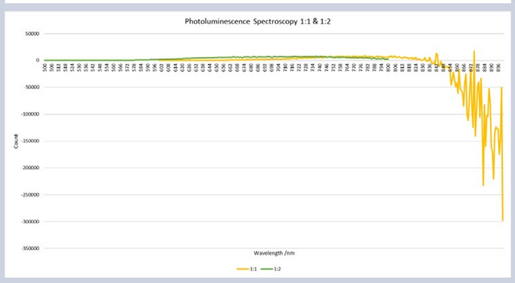
2 Aims and Objectives

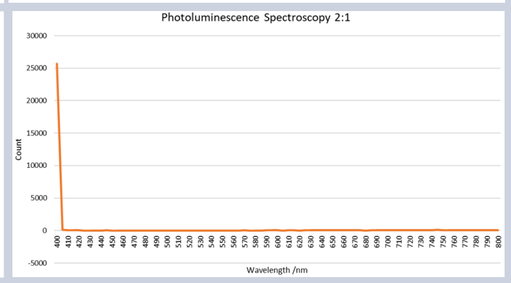
To test the validity of the method of synthesising QD solid thin films of n- and p-type NC's by surfactant driven self-assembly and characterise the produced crystals. These were achieved by:

- The synthesis of 1:1; 2:1 and 1:2 Cu:In NC's in solid and liquid forms
- Deposition of the liquid solution of NC's onto glass substrates
- Characterisation of the NC's using X-ray diffraction (XRD) and various spectroscopy methods









1. Graph describing the intensity of X-rays received after diffracting through the 2:1 and 1:2 dry samples
2. Graph describing the absorbance of light in the 2:1 and 1:2 wet samples after subtracting from the hexane reference spectra
3. & 4. Graphs describing the photoluminescence spectra of the wet samples; 1:1 and 1:2 on 3; 2:1 on 4

3 Methodology

Crystal Synthesis

- The NC's were synthesised in three separate batches for the three different NC ratios. These were measured by mass using indium acetate and copper (I) iodide powders, mixed together before adding to the tri-neck flask. Octadecene and dodecanethiol were added as solvents and to prevent defects forming in the flask.
- Each batch was subjected to a nucleation reaction with a steadily increasing temperature reaching a maximum of approximately 210ºC. A constant nitrogen supply and a spinning magnet was placed into the flask to ensure a consistent mixture at all stages of the reaction.
- Once the solution had been left to rest, for a minimum of 15 minutes to allow for adequate crystal growth, the solution was slowly cooled to 30ºC, using nitrogen.
- The flask containing the mixture was removed from its position and the solution itself was removed by pipette into a separate air-tight bottle

Crystal Cleaning

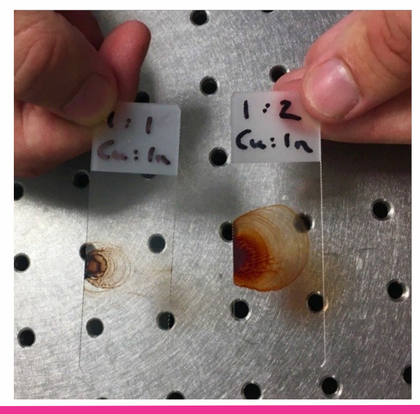
- Hexane was added to the solution by pipette, using different pipettes for the solutions of different ratios, then the sum was divided into two equal samples.
- Approximately 30ml of methane and chloroform was added to each sample.
- The samples were placed in a centrifuge then spun at 7830rpm for 5 minutes. The waste product was removed and the difference was replaced with more hexane. This process was repeated for a second spin, with the remaining solutions transferred over to storage bottles.
- The solvent of each solution (wet samples) was separated from the solute (dry samples).

The dry samples were left to dry completely for X-ray Diffraction (XRD) to avoid vaporisation in the vacuum, to determine it's atomic structure and thus test the validity of the method of synthesis.

The wet samples were tested using photoluminescence spectroscopy to reveal it's electronic structure through the incidence and emission of light and ultraviolet-visible light spectroscopy to understand further it's optical properties.

4 Results

- **XRD –** The two samples 2:1 and 1:2, used for contrast, show very little variation from one another. The broad peaks of the graph occur around 5º, 24º and 44º with no significantly sharp increases, indicating a nanoscale crystal being produced with the expected chemical composition. The average size can be calculated using the Scherrer formula [2] $Dp = (0.94 \times \lambda) / (\beta \times \cos\Theta)$. This results in sizes of 101.39nm for 2:1 and 101.40nm for 1:2 at 5º, the highest peaks following the continuous initial drop in intensity.
- **Ultraviolet-Visible –** The same two samples, again used for contrast, verify the visible colour of the liquid sample of being a dark red, as it is highest at a smaller wavelength, towards infra-red end of the Electromagnetic Spectrum. The largest gap in absorbance rate occurs at 500nm with the 1:2 sample above and at 595nm 2:1 is above. This also follows predictions as 1:2 is brighter under an ultraviolet lamp.
- **Photoluminescence –** The 2:1 sample shows a dramatically different pattern to either 1:1 or 1:2, with an almost flat line from 406nm onwards whereas 1:1 is extremely volatile from 841nm onwards, showing the huge difference in illumination an increased amount of copper produces.



5 Conclusion

Overall, the aims of this project have been met as the method used has reliably produced nanocrystals of a practical size and accurate composition across all three samples.
The greater the amount of copper in a crystal, the weaker it interacts with light sources with a longer wavelength, indicating indium interacts more strongly with electromagnetic fields.
Opportunity for further research remains to clarify these findings.

References

[1] B. Chen *et al,* "Highly Emissive and Color-Tunable CuInS2-Based Colloidal Semiconductor Nanocrystals: Off-Stoichiometry Effects and Improved Electroluminescence Performance," *Adv. Funct. Mater. Jnl*., 2012.

[2] "XRD Crystallite Size Calculator (Scherrer Equation)", *InstaNANO,* 2019. [Online] Available: https://www.instanano.com/2017/01/xrd-crystallite-size-calculator-scherrer-equation.html

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