

# Nickel Sulfide Nanocrystal Synthesis Using Substituted Thiophenols

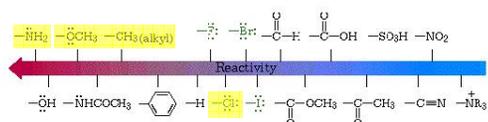
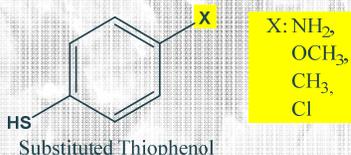
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## Introduction

Different phases and morphologies can largely effect the catalytic abilities of nickel sulfide nanocrystals. While nickel sulfides contain an abundance of different phases, phase control of these crystals can be difficult. One proposed method of selectively isolating these phases involves manipulating the sulfur reagent used, where the electron donating ability of substituent groups influences the reactivity of the sulfur precursor. Para-substituted thiophenols were used as the sulfur for this work.

### Sulfur reagents used in this synthesis:



Electron Donating Group (EDG)      Electron Withdrawing Group (EWG)

Bruce, P. Y. (2004). Organic Chemistry 6<sup>th</sup> Edition. Upper Saddle River, NJ: Pearson/Prentice Hall

### Potential Phases: Nickel Oxidation States:

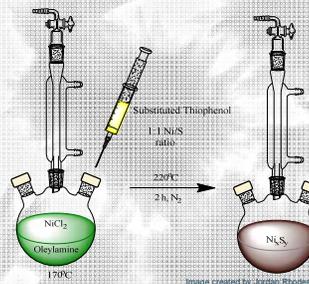
- Starting Material (NiCl<sub>2</sub>)      Ni<sup>+2</sup>
- Heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>)      Ni<sup>+1</sup>Ni<sup>+3</sup>Ni<sup>+2</sup>
- Polydymite (Ni<sub>3</sub>S<sub>4</sub>)      Ni<sup>+3</sup>Ni<sup>+3</sup>Ni<sup>+2</sup>

### Proposed hypothesis for phase change:

Electron donating groups are able to donate electrons to the nickel atoms, lowering nickel's oxidation state, while electron withdrawing groups take electrons and raise the oxidation state.

## Synthetic Process

- Oleylamine was used as the solvent of the reaction, its steric effects are used to help control particle size.
- The para-substituted thiophenol was injected into the nickel solution at 170°C, to form a precursor phase, then heated to 220°C to form the desired phase.



A 1:1 ratio of Ni:S eliminated the thermodynamically stable millerite phase (NiS) consistently found creating mixed phase products when larger quantities of sulfur were present.

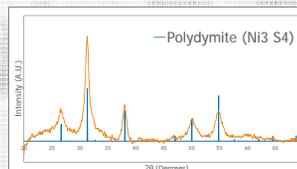
## Phase Characterization

X-Ray Diffraction (XRD) was used to analyze the phase composition of each of the particles.

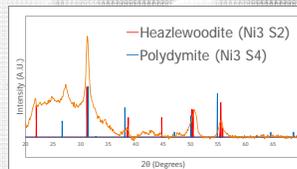
Phase	Phase
Cl	Polydymite (Ni <sub>3</sub> S <sub>4</sub> ) – 100%
CH <sub>3</sub>	Polydymite (Ni <sub>3</sub> S <sub>4</sub> ) – 71.6% Heazlewoodite (Ni <sub>3</sub> S <sub>2</sub> ) – 28.4%
OCH <sub>3</sub>	Polydymite (Ni <sub>3</sub> S <sub>4</sub> ) – 52.9% Heazlewoodite (Ni <sub>3</sub> S <sub>2</sub> ) – 47.1%
NH <sub>2</sub>	Heazlewoodite (Ni <sub>3</sub> S <sub>2</sub> ) – 100%

EWG

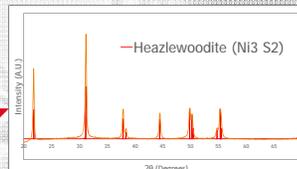
Cl



CH<sub>3</sub>



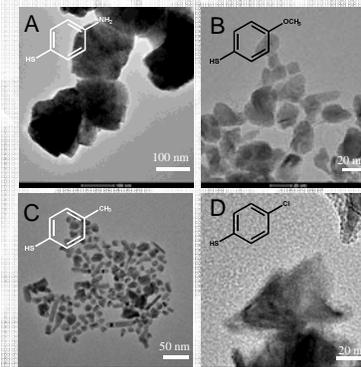
NH<sub>2</sub>



EDG

Sulfur rich nickel sulfide phases correlated to substituted thiophenols with the less electron donating groups.

## Morphological Characterization



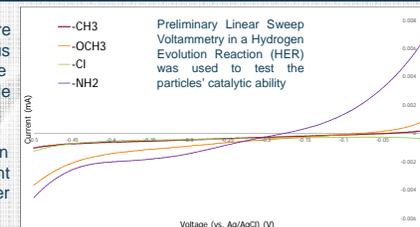
TEM images taken by Jordan Rhodes

- Transmission Electron Microscopy (TEM) was used to obtain these images.
- A-D decreases in terms of electron donating groups, A being the most electron donating and D being the least.
- A larger surface area to volume ratio (smaller particles with more edges) typically makes for a better catalyst.

## Testing Catalytic Ability

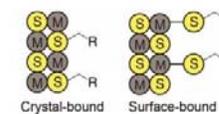
A more positive voltage when the current drops indicates particles with better catalytic abilities.

While the results are preliminary and thus inconclusive, there is already a possible trend showing particles formed using more electron donating substituent groups have greater catalytic abilities.



## Future Direction and Conclusion

We have developed a facile synthesis of nickel sulfide nanocrystals through hot injection that demonstrates phase control by varying the substituent group of para-substituted thiophenols. In the future, we look to further test and enhance the particles catalytic abilities and test to see if the ligands on the particles are surface or crystal bound.



Turo M.J., Macdonald M.E., ACS Nano, 2014, 8 (10), pp 10206

Crystal bound ligands are far more desirable as catalysts because they leave the metal sites of nanocrystals exposed, the catalytically active centers. Additionally crystal bound ligands are more tightly bound and less likely to break. The ligands won't contaminate the reaction solution.

## Acknowledgements

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