

UNIVERSITY OF TECHNOLOGY SYDNEY

DOCTORAL THESIS

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**Thiol-Mediated Synthesis of  
Transition Metal and Transition  
Metal Sulfide Nanowires**

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*Author:*

John SCOTT

*Supervisor:*

Prof. Milos TOTH

*A thesis submitted in fulfillment of the requirements  
for the degree of Doctor of Philosophy*

*in the*

Materials and Technology for Energy Efficiency  
School of Mathematical and Physical Sciences

February 26, 2019

## Declaration of Authorship

I, John SCOTT, declare that this thesis titled, "Thiol-Mediated Synthesis of Transition Metal and Transition Metal Sulfide Nanowires" and the work presented in it are my own. I confirm that:

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*“Like sittin’ on pins and needles, things fall apart, it’s scientific”*

David Byrne



University of Technology Sydney

# *Abstract*

Faculty of Science  
School of Mathematical and Physical Sciences

Doctor of Philosophy

## **Thiol-Mediated Synthesis of Transition Metal and Transition Metal Sulfide Nanowires**

by John SCOTT

In this work, I discuss my investigation into the bottom-up synthesis of metal and metal sulfide nanowires supported by a capping reagent. Capping reagents are chemical species that alter the crystal growth kinetics. Through their deployment, the scalable synthesis of low-symmetry nanocrystals (such as nanowires) can be achieved. Here, I show the synthesis of metal (Co, Ni) and binary metal sulfide ( $\text{Co}_9\text{S}_8$ ,  $\text{Ni}_3\text{S}_2$ ) nanowires by heat-up thermolysis of simple molecular precursors. Detailed analysis of the precursors and the reaction steps leading to nanowire growth is provided. The unusual reaction conditions enable new insights through *in situ* characterisation using thermogravimetry with evolved gas analysis and field-emission scanning electron microscopy. This provides new understanding of the precursor conversion rates and identification of active chemical species that support 1D growth. To confirm the role ligand fragments play in shaping the crystal growth kinetics, substitution of the precursors was performed. It is further shown that anisotropic growth can selectively be tuned by deployment of the capping ligand species. Based on these new understandings, the high-yield synthesis of technologically important  $\text{Co}_9\text{S}_8$  nanowires by chemical vapour deposition is presented.



## *Acknowledgements*

I would like to express my deepest thanks to Professor Milos Toth. I am sincerely grateful for the knowledge and support you have provided during this work. I would also like to thank Associate Professor Charlene Lobo and Professor Igor Aharonovich. Each day I am part of a wonderful environment to learn and explore.

My sincerest thanks to Mr. Geoff McCredie, Mrs. Katie McBean and Mr. Mark Berkahn for your support over the course of my project. To Associate Professor Andrew McDonagh and Alexander Angeloski who have provided exceptional guidance and help with analysis of the precursor compounds and editing of manuscripts. To my fellow students, I would like to thank all of you for your friendship. A special thank you to Toby Shanley, Chris Elbadawi, Alexander Angeloski, Toan Tran and Noah Mendelson for allowing me to collaborate with you on your research projects. James Bishop and Aiden Martin for assistance with time-dependent SEM characterisation during nanowire growth. To James Bishop, Aiden Martin, Chris Elbadawi and Mehran Kianinia for all the work you have done in setting up the lab.

A special thanks to my family and my love Vanessa for the support you have showed me in my life. Lastly and most of all I would like to thank my mum Ellie. Your support, encouragement and love made this work possible.



# Publications

## Contributing Publications

- Solventless synthesis of  $\text{Co}_9\text{S}_8$ ,  $\text{Ni}_3\text{S}_2$ , Co and Ni nanowires, **J. A. Scott**, A. Angeloski, I. Aharonovich, C. J. Lobo, A. McDonagh and M. Toth, *Nanoscale*, 2018 (submitted)
- Versatile method for template-free synthesis of single crystalline metal and metal alloy nanowires, **J. A. Scott**, D. Totonjian, A. A. Martin, T. T. Tran, J. Fang, M. Toth, A. M. McDonagh, I. Aharonovich, C. J. Lobo, *Nanoscale*, 2016, 8(5), 2804-2810.

## Non-contributing Publications

- Engineering and Tuning of Quantum Emitters in Few-Layer Hexagonal Boron Nitride, N. Mendelson, Z.Q. Xu, T. T. Tran, M. Kianinia, **J. A. Scott**, C. Bradac, I. Aharonovich and M. Toth, *ACS Nano*, 2019
- Conversion of single crystals of a nickel(II) dithiocarbamate complex to nickel sulfide crystals, A. Angeloski, M. Cortie, **J. A. Scott**, D. Bordin, A. M. McDonagh, *Inorganica Chimica Acta*, 2019, 487, 228-233
- From Lead (II) Dithiocarbamate Precursors to a Fast Response PbS Positive Temperature Coefficient Thermistor, A. Angeloski, A. R. Gentle, **J. A. Scott**, M. B. Cortie, J. M. Hook, M. T. Westerhausen, M. Bhadrhade, A. T. Baker, A. M. McDonagh, *Inorganic Chemistry*, 2018, 57(4), 2123-2140.
- Electron beam microscope with improved imaging gas and method of use, T. Shanley, **J. A. Scott**, and M. Toth, U.S. Patent 9,633,816 (2017)
- Room-Temperature Single-Photon Emission from Oxidized Tungsten Disulfide Multilayers, T. T. Tran, S. Choi, **J. A. Scott**, Z.Q. Xu, C. Zheng, G. Seniutinas, A. Bendavid, M. S. Fuhrer, M. Toth, I. Aharonovich, *Advanced Optical Materials*, 2017, 5(5).
- Role of Gas Molecule Complexity in Environmental Electron Microscopy and Photoelectron Yield Spectroscopy, T. W. Shanley, F. Bonnie, **J. A. Scott**, M. Toth, *ACS Applied Materials & Interfaces*, 2016, 8(40), 21305-27310.

- Electron beam directed etching of hexagonal boron nitride, C. Elbadawi, T. T. Tran, M. Kolíbal, T. Šíkola, **J. A. Scott**, Q. Cai, L. H. Li, T. Taniguchi, K. Watanabe, M. Toth, I. Aharonovich and C. Lobo, *Nanoscale*, 2016, 8(36), 16182-16186.

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# List of Abbreviations

<b>TEM</b>	<b>T</b> ransmission <b>E</b> lectron <b>M</b> icroscope
<b>EDS</b>	<b>E</b> nergy <b>D</b> ispersive ( <b>X</b> -ray) <b>S</b> pectroscopy
<b>NMR</b>	<b>N</b> uclear <b>M</b> agnetic <b>R</b> esonance
<b>SEM</b>	<b>S</b> canning <b>E</b> lectron <b>M</b> icroscope
<b>FESEM</b>	<b>F</b> ield <b>E</b> mission <b>S</b> canning <b>E</b> lectron <b>M</b> icroscope
<b>FTIR</b>	<b>F</b> ourier- <b>T</b> ransform <b>I</b> nfra <b>R</b> ed (spectroscopy)
<b>SAED</b>	<b>S</b> electe <b>A</b> <b>E</b> lectron <b>D</b> iffraction
<b>XRD</b>	<b>X</b> - <b>R</b> ay <b>D</b> iffraction
<b>UV-vis</b>	<b>U</b> ltraviolet <b>V</b> isible <b>S</b> pectroscopy
<b>DTG</b>	<b>D</b> ifferential <b>T</b> hermal <b>G</b> ravimetric analysis



*Dedicated to my mum...*

