UNIVERSITY OF TECHNOLOGY SYDNEY

DOCTORAL THESIS

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

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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:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- This research is supported by an Australian Government Research Training Program Scholarship.
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- I have acknowledged all main sources of help.
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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 (Co_9S_8, Ni_3S_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 Co_9S_8 nanowires by chemical vapour deposition is presented.

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Publications

Contributing Publications

- Solventless synthesis of Co_9S_8, Ni_3S_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. Bhadbhade, 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. Šikola, **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

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

Dedicated to my mum…