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

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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
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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
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$_9$S$_8$, Ni$_3$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 Co$_9$S$_8$ nanowires by chemical vapour deposition is presented.
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**Publications**

**Contributing Publications**

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<tbody>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive (X-ray) Spectroscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field Emission Scanning Electron Microscope</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-Transform InfraRed (spectroscopy)</td>
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<td>Selected Area Electron Diffraction</td>
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<tr>
<td>DTG</td>
<td>Differential Thermal Gravimetric analysis</td>
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Dedicated to my mum…