

## Single Reagent Synthesis of Copper Sulfide Nanoparticles in Water

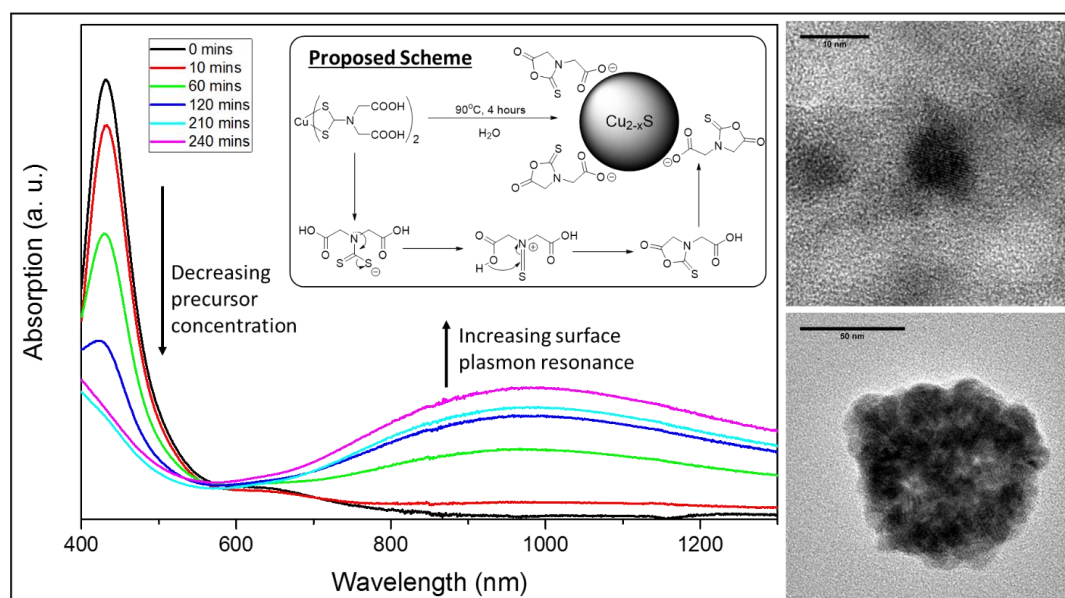
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Colloidal copper-based nanomaterials are being researched extensively for a range of applications from energy generation to diagnostics and therapy<sup>1</sup>. Plasmonic copper sulfide ( $\text{Cu}_{2-x}\text{S}$ ) nanoparticles in particular are of interest for biomedical use, with the potential for photoacoustic imaging and photothermal therapy, requiring engineered biocompatibility<sup>2</sup>. Here we present the preparation of a water soluble copper dithiocarbamate complex and its use as a self-capping precursor for the aqueous synthesis of colloidal  $\text{Cu}_{2-x}\text{S}$  nanocrystals. The dithiocarbamate ligand chosen for this reaction (Figure 1) supplies not only the sulfur required for nanocrystal formation but may also provide the capping ligand necessary for colloidal stability. Self-capping precursors based on dithiocarbamates have previously been described for the synthesis of hydrophobic CdS nanocrystals<sup>3</sup>. Figure 1 includes an outline of the proposed reaction scheme and mechanism of formation of the decomposition product capable of acting as a capping ligand. This mechanism is based on previous work that used cadmium dithiocarbamates to synthesise CdS nanocrystals in water, in which the decomposition product was identified and crystal structure obtained<sup>4</sup>. Our work aims to prepare  $\text{Cu}_{2-x}\text{S}$  nanocrystals in aqueous solution from a single precursor molecule and characterise the resulting nanocrystals and capping ligand.



**Fig. 1** Clockwise from top: a proposed scheme for the thermal decomposition of a water soluble copper dithiocarbamate complex; TEM images of both a single, 8 nm  $\text{Cu}_{2-x}\text{S}$  nanocrystal and an aggregate  $\text{Cu}_{2-x}\text{S}$  structure with a diameter of ca. 80 nm; and the absorption spectra acquired during the growth of  $\text{Cu}_{2-x}\text{S}$ .

The water soluble copper dithiocarbamate complex was prepared and its structure confirmed with positive mode ESI mass spectrometry. After isolation, the complex was decomposed at 90°C in water over 4 hours to give colloidal  $\text{Cu}_{2-x}\text{S}$  nanocrystals in the absence of any additional capping ligand. TEM images confirmed the presence of  $\text{Cu}_{2-x}\text{S}$  nanocrystals ca. 8 nm in diameter with clear lattice fringes but indicated the majority of these nanocrystals had aggregated to give structures with an average diameter of 80 nm. This was confirmed through DLS measurements that reported an average hydrodynamic diameter of 96 nm and a polydispersity index of 0.10. Absorption spectroscopy exhibited a decrease in the absorption at 430 nm due to the precursor copper complex and the appearance of a broad absorption centred around 1000 nm. This peak in the near infrared (NIR) can be attributed to the localised surface plasmon resonance (LSPR) of copper sulfide nanoparticles. Preliminary photothermal experiments support the use of these nanoparticles for localised heating through the absorption of NIR light. Further work will be carried out to compare these  $\text{Cu}_{2-x}\text{S}$  samples to those synthesised in the presence of an additional capping ligand. An excess of additional capping ligand may allow for the aqueous synthesis of smaller, more monodisperse  $\text{Cu}_{2-x}\text{S}$  nanocrystals.

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