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Taking Bismuthinite to Bismuth Sulfide Nanorods in Two Easy Steps

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The transformation of mineral bismuthinite, to Bi₂S₃ nanoparticles, via a simple two-step process is described. The reaction of bismuthinite with two aryldithioic acids gave the complexes; [Bi(S₂C(C₆H₄)-4-CH₃)₃] and [Bi(S₂C(C₆H₄)-4-OCH₃)₃]. Mild solution decomposition (120 °C) of these bismuth aryldithioates produced crystalline Bi₂S₃ nanorods.

Bismuth sulfide (Bi₂S₃) has important intrinsic physical and electronic properties.¹ It is a well-known lamella structured V-VI semiconductor material with a direct band gap in the range of 1.3 – 1.7 eV.^{2,3} Bi₂S₃ has been used as a thin film material in photodiode arrays, photovoltaic devices and thermoelectric cooling devices.^{4,5}

Recent research has focused on the synthesis and applications of one-dimensional Bi₂S₃ nanomaterials due to reported enhancement of thermal, electric and optoelectronic properties.^{4,6,7} A variety of nanostructures have been investigated for use in nanoscale devices,^{8,9} CT imaging,^{10,11} high energy dosimetry (ie: radiation detection),¹² gas sensing^{7,13,14} and hydrogen storage.¹⁵ Furthermore, Bi₂S₃ nanomaterials are considered to be relatively non-toxic and environmentally compatible when compared to other semiconductors within the same group.^{1,16–18}

Several techniques have been reported for the synthesis of Bi₂S₃ nanoparticles; solvothermal^{9,15} and hydrothermal¹⁹ decomposition, microwave irradiation,^{20,21} crystallisation of amorphous colloids,²² chemical vapour deposition,⁸ biomolecule assisted approaches,¹⁰ mechanochemical synthesis¹⁷ and sonochemical methods.²³ These rely primarily on the isolation of defined bismuth complexes incorporating S-based ligands as single source precursors, or the *in-situ* reaction and decomposition of a mixture of the bismuth and sulfur-containing reactive components. The S-based ligands are normally drawn from; thiocarboxylates,^{24,25}

thiocarbamates,²⁶ thiosemicarbazides,²⁷ thiophosphates,¹⁵ thiolates,²⁸ xanthates,^{29,30} thioacetamide,^{31,32} thiourea,^{20,27,33} glutathione,³⁴ cysteine,⁹ Na₂S,³⁵ as well as elemental sulfur,^{8,17,36} while the bismuth(III) sources are preformed bismuth salts; Bi(NO₃)₃,^{19,20,33} BiCl₃,³² Bi₂(SO₄)₃¹⁶ and Bi(O₂CCH₃)₃,³⁶ as well as bismuth powder.¹⁷

Bismuthinite is the mineral form of bismuth sulfide. It is grey-metallic in colour, is brittle, dense and of little industrial or commercial use except for the extraction of bismuth metal. Bismuth sulfide is known to react with strong mineral and oxidising acids (HCl, HNO₃ and H₂SO₄) to generate the respective bismuth salts. However, it is generally unreactive towards organic acids severely hampering its use in chemical synthesis. Thus, despite extensive research into the formation of nanostructured bismuth sulfide, there have been no reports of Bi₂S₃ being used as a starting material in the formation of any metal-organic bismuth(III) compounds and subsequently in the controlled formation of bismuth sulfide nanoparticles. To our knowledge there has only been a single report exploring the use of a combination of Bi₂S₃ and elemental sulfur in the high temperature (650 °C) chemical vapour deposition of Bi₂S₃ nanoflowers.⁸

We have discovered that aryldithioic acids (ArCS₂H) will react quickly and effectively with crude bismuthinite as a heterogeneous mixture in toluene under sonication to generate the respective bismuth(III) aryldithioates, [Bi(S₂CAR)₃] in almost quantitative yield. The reaction pathway is shown in Scheme 1 for both 4-methylbenzodithioic and 4-methoxybenzodithioic acids.

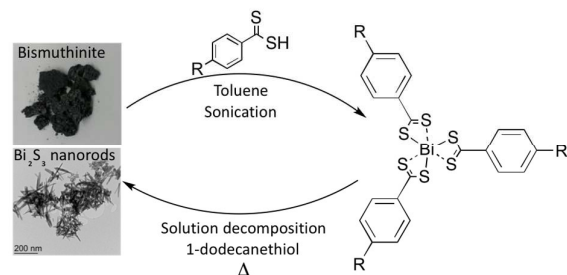
This provides for a simple and direct route from bismuthinite to well formed bismuth sulfide nanoparticles in two easy steps, and can actually be achieved in a single-pot reaction.

As an illustrative example, insoluble bismuthinite (Bi₂S₃) is added to a bright red toluene solution of 4-methylbenzodithioic acid in a 1:6 stoichiometry. The heterogeneous mixture is sonicated for between 4 – 6 hr until all the grey-black colour of the bismuthinite is replaced by a red/brown precipitate.

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† Footnotes relating to the title and/or authors should appear here.

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Scheme 1: Synthesis of Bi_2S_3 nanostructures from bismuthinite, in two simple steps. Where R is CH_3 (**1**) or OCH_3 (**2**).

Note: This will slowly generate toxic H_2S *in situ* and all necessary precautions should be taken. The solid is collected by filtration, washed with a small aliquot of toluene to remove any unreacted acid, and air-dried. The solid can then be easily recrystallised from hot toluene, though it is also soluble in THF, chloroform, acetone and DMSO.

Thus, complexes $[\text{Bi}(\text{S}_2\text{C}(\text{C}_6\text{H}_4)\text{-4-CH}_3)_3]$ **1** and $[\text{Bi}(\text{S}_2\text{C}(\text{C}_6\text{H}_4)\text{-4-OCH}_3)_3]$ **2**, were isolated as air-stable, crystalline solids. Elemental analysis, FT-IR, ^1H and ^{13}C NMR and mass spectrometry confirmed the composition of the crystals. This data is provided in full in the Supporting Information (ESI).

The solid-state structure of **1** was determined by single crystal X-ray diffraction, however crystals of **2** were consistently twinned and provided poor diffraction data. Crystals suitable for X-ray diffraction studies of compound **1** were grown from a toluene solution. A summary of the crystallographic data for **1** is provided in the ESI. Complex **1** (Figure 1) contains one Bi(III) atom bound to three aryldithioate ligands giving an overall distorted pentagonal pyramidal geometry. The dithioate ligands are chelated to the central Bi(III) atom in an asymmetrical fashion with distinct short (Bi-S average 2.695 Å) or long (Bi-S average 2.888 Å) bond lengths which fall into the same range as those seen in other similar Bi(III) dithioate complexes $[\text{Bi}(\text{S}_2\text{CPh})_3]$,³⁷ $[\text{BiCH}_3\{\text{S}_2\text{C}(4\text{-MeC}_6\text{H}_4)\}_2]$ ²⁴ and $[\text{BiPh}\{4\text{-OMeC}_6\text{H}_4\}_2]$.³⁸ Two of the dithioate chelated ligands are close to coplanar ($\pm 4.6790(16)$ Å) with the third ligand lying almost orthogonal. This apical ligand [S(1) S(2)] has slightly exaggerated asymmetry in its Bi-S bonds when compared to the other two chelating ligands. Looking at the extended crystal packing arrangement in **1** (Figure 1 and Figure S3), there is a long Bi-S intermolecular interaction [Bi(1)-S(6') 3.5052(8) Å] that is significantly shorter than the sum of the *van der Waals* radii of both atoms (Bi-S 4.25 Å),³⁹ allowing a final zigzag polymeric chain to form.

Bi_2S_3 nanorods were generated through decomposition of either **1** or **2** in mesitylene, in the presence of 1-dodecanethiol or 1-octadecanethiol, according to published methods.^{27,40}

Transmission electron microscopy (TEM), selective area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDS) confirmed the isolation of Bi_2S_3 nanorods. The individual nanorods have diameters averaging 7-10 nm

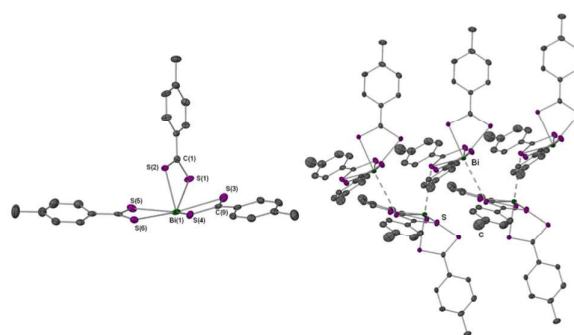


Figure 1: Molecular structure of $[\text{Bi}\{\text{S}_2\text{C}(4\text{-MeC}_6\text{H}_4)\}_3]$ **1** (ASU on left, extended packing section on right) showing thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Bi(1)-S(1), 2.9119(8); Bi(1)-S(2), 2.5787(8); Bi(1)-S(3), 2.8487(9); Bi(1)-S(4), 2.7282(8); Bi(1)-S(5), 2.9063(9); Bi(1)-S(6), 2.7792(8); S(1)-Bi(1)-S(2), 64.23(2); S(3)-Bi(1)-S(4), 63.43(2); S(5)-Bi(1)-S(6), 62.19(2); Bi(1)-S(6)', 3.5052(8).

and lengths up to >200 nm (Figure 2). The average length of the nanorods is more difficult to determine due to their slightly aggregated state. High resolution TEM imaging shows the crystalline nature of the sample, with clear lattice fringes observed in Figure 2. The SAED patterns (Figure S4) again indicate the highly crystalline nature of the sample and could be indexed to the orthorhombic phase of bismuth sulfide (JCPDS card No. 17-0320, $a=11.15$ Å, $b=11.31$ Å and $c=3.98$ Å). EDS microanalysis established the presence of bismuth and sulfur in the nanorods and the Bi, S atomic percentages were suggestive of a Bi_2S_3 composition (Figures S5 and S6).

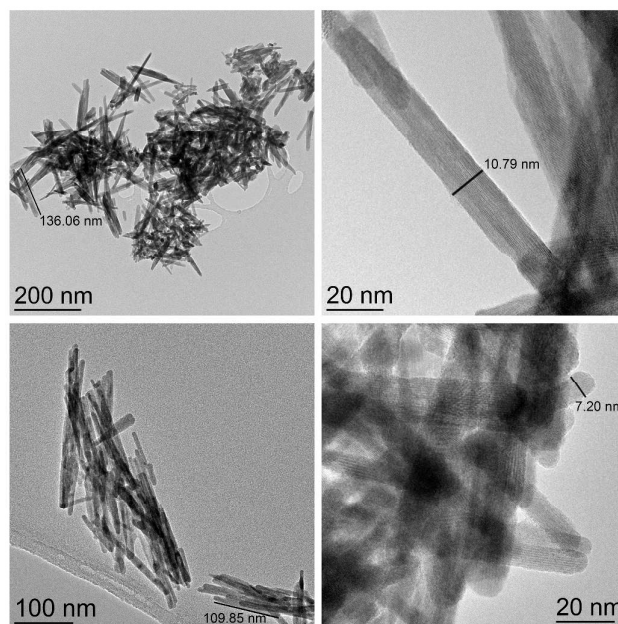


Figure 2: TEM images of the Bi_2S_3 nanorods isolated from the solution decomposition of **1** (top) and **2** (bottom).

Although two different surfactants were used (1-dodecanethiol or 1-octadecanethiol) the morphologies of the Bi_2S_3 nanorods were not significantly different. Surfactants generally act as a capping agents, which can reduce the growth of the nanocrystal in a certain direction and/or prevent agglomeration.³¹ Due to the thiophilic nature of bismuth, these sulfur-containing surfactants are likely to have a strong capping capability. Previous studies ascribe the observed one-dimensional nanorod formation to the presence of these sulfur-containing surfactants.²⁷

As mentioned earlier, this procedure is amenable to a one-pot process. All reagents were used in the same ratios and combined in one pot. The consumption of mineral Bi_2S_3 and formation of **2** was observed by a colour change from grey-black to red. The Bi(III) complex was not isolated but simply decomposed *in situ* (see ESI for full details). The morphology of the resulting Bi_2S_3 nanorods was similar to those formed from the two-step process (Figure S7), however the one-pot sample appeared to contain (many) larger aggregates of small nanorods.

In summary, we have discovered a novel method for converting crude bismuthinite to crystalline Bi_2S_3 nanorods, via a mild and simple two-step process.

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Table of Contents

Treatment of bismuthinite with aryldithioc acids under sonication leads easily to the formation and isolation of bismuth(III) aryldithioate complexes $[\text{Bi}(\text{S}_2\text{CAr})_3]$ which decompose readily to give well formed Bi_2S_3 nanorods.

