Processing and characterisation of Mo₆S₂I₈ nanowires†

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One-dimensional nanostructures based on the Mo–S–I system have recently aroused a lot of interest as a viable alternative to the ubiquitous carbon nanotube due to their uniform structure and electronic properties for a given composition. Previous research on the Mo₆S₃I₆ and Mo₆S_{4.5}I_{4.5} stoichiometries has also shown them to be soluble in common solvents like water, acetone or isopropyl alcohol, and to debundle on dilution. Here, the solubility, debundling and composition of Mo₆S₂I₈ nanowires are presented. They were found to be most soluble in dimethylformamide, which retained 47 wt% of a 0.08 g l^{−1} nanowire (NW) material dispersion as thin NW bundles after one week. Dispersions of 0.8 g l^{−1} and 5 g l^{−1} even retained 54 wt% and 66 wt%, respectively. However the NW material was completely insoluble in water, and the surface energy of Mo₆S₂I₈ NWs was deduced as 67 mJ m^{−2}, higher than for other Mo–S–I NWs. UV-vis-NIR spectroscopy showed nanowire peaks familiar from Mo₆S₃I₆ and Mo₆S_{4.5}I_{4.5} spectra around 1.8 and 2.8 eV, as well as unforeseen ultraviolet peaks at 3.5 and 4.4 eV. These chemical differences suggest an alternate, more strongly bonded structure to that seen for Mo₆S₃I₆ and Mo₆S_{4.5}I_{4.5} NWs. Films deposited from a range of concentrations were investigated using atomic force microscopy (AFM) to determine bundle diameter distributions. The average diameter and the spread in diameters were found to decrease somewhat with decreasing concentration. However extrapolation gave a finite bundle size at infinite dilution, and an extension of the existing debundling model is proposed to take this into account. To confirm the nominal stoichiometry of Mo₆S₂I₈, which does not follow the generic Mo₆S_xI_{9−x} formula of previous stoichiometries, EDX was carried out. The composition of nanowire bundles was found to be Mo₆S_{2.3}I_{8.6}, supporting the nominal composition.

1. Introduction

One-dimensional nanostructures based in the Mo–S–I system have recently aroused a lot of interest as a viable alternative to carbon nanotubes for a range of nanotechnological applications. Mo₆S_xI_{9−x} nanowires (NWs) are particularly promising because they can be synthesised in a one-step process,^{1–3} and are readily purified in common solvents such as 2-propanol or acetone,^{4,5} resulting in a stable solution of NW bundles. While the bundle length can only be altered during the growth process and through sonication of dispersions of the as-grown material,⁴ the mean diameter of the bundles in solution can be tuned by dilution, with large fractions of individual NWs attainable at concentrations around 1 mg l^{−1}.^{5,6} The NWs possess high Young's moduli but low shear moduli,⁷ making them viable for mechanical composites. They have also been

added to polymers as conductive fillers, exhibiting an ultra-low percolation threshold of 2×10^{-5} .⁸ NWs themselves have the same electronic properties for a given composition,¹ making them easier to use than carbon nanotubes for electronics applications. In particular, Mo₆S₃I₆ NW bundles have electrical conductivities of up to 10 Sm^{−1},⁹ and conductivities up to 15 000 Sm^{−1} have been measured for single NWs³. They can be aligned using dielectrophoresis,⁹ and efficiently connected to gold nanoparticles or green fluorescent proteins simply by mixing aqueous solutions of both species.¹⁰

Finally, they are stable in air up to 350 °C,¹ and exhibit good field emission¹¹ and lubricating properties.¹² The two Mo₆S_xI_{9−x} NW stoichiometries that have been researched so far, nominally Mo₆S₃I₆ and Mo₆S_{4.5}I_{4.5}, exhibit many exciting properties, as well as excellent processability. Recently, Mo₆S₂I₈, which has been known as a compound for some time,¹³ has also been synthesised in NW form. We anticipate entirely new properties as these NWs do not seem to follow to generic Mo₆S_xI_{9−x} formula; that is, because $2 + 8 \neq 9$. In this paper we show how these NWs can be processed, and ascertain whether the nominal stoichiometry is correct.

2. Experimental method

Mo₆S₂I₈ NW material synthesised from the constituent elements was obtained from Mo6 d.o.o and washed with acetone to remove the unreacted iodine. Dispersions of 0.7 mg of this raw

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material in 9 ml solvent were prepared for the following solvents: acetone, benzyl alcohol (BA), chloroform (CHCl₃), dimethyl acetamide (DMAc), dimethyl formamide (DMF), ethanol, gamma-butyrolactone (GBL), 2-propanol (IPA), *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), toluene and water. All dispersions were first sonicated for 5 min using a hielscher UP100H ultrasonic tip (50 W, 30 kHz), then for 2 h in an Ultrawave U50 ultrasonic bath (100 W, 42 kHz), followed by another 5 min using the ultrasonic tip.

Each dispersion was then transferred to a 1 cm path length quartz cuvette, and the transmission of laser pulses ($\lambda = 650$ nm, pulse duration 10 ms) through the centre of the sample was monitored over the course of a week. Sedimentation equations¹⁴ were fitted to the data to determine the number of sedimenting phases, and their time constants τ .

Fresh dispersions were subsequently prepared, and the different sediments decanted at time 4τ (at which it was assumed that none of that sedimenting phase remained in solution). Each sediment, and the solute that remained in solution, were deposited on 400 mesh holey carbon on copper grids and imaged with JEOL 2000FX and JEOL 2010 transmission electron microscopes (TEM) operated at 200 kV. A dilution series of the solute that remained in DMF was prepared, as well as dispersions of raw material in DMF at concentrations ranging from 1 to 0.001 g l⁻¹. UV-vis-NIR absorbance spectra from 200–2200 nm were acquired for both using a Varian Cary 5000 Spectrometer, at 600 nm min⁻¹. Spectra from the different phases in DMF isolated for the aforementioned TEM study were also acquired. Solute in DMF at different concentrations was deposited on cleaved mica substrates and bundle size distributions measured with a Park Scientific Instruments Autoprobe CP atomic force microscope (AFM) operated in tapping mode using a Mikromash NSC35/AlBS tip (silicon, tip radius 10 nm, $k = 4.5$ N m⁻¹, $\omega = 150$ kHz). The amount of solute in the best solvent (DMF) was measured by preparing dispersions at 0.08, 0.8 and 5 g l⁻¹, allowing all sediments to settle out, and decanting the remaining solution. These solutions were centrifuged with a SIGMA 3–18 centrifuge at 12 000 rpm, and dried in a Shellab EV018 vacuum oven at 80 °C to get rid of the solvent (the solute was weighed every hour, up until a stationary weight was reproducibly weighed. The weight stabilised after 3 h of drying time, suggesting that there was no solvent to evaporate anymore). The solute thus obtained from the 0.08 g l⁻¹ and 0.8 g l⁻¹ dispersions was weighed using the balance of a Perkin Elmer Pyris Thermogravimetric Analyser. Quantification of molecular molybdenum species and nanoparticles in dispersion was performed. A dispersion of the NW material in acetone was passed through a 0.2 micrometer pore size polytetrafluoroethene (PTFE) filter membrane several times. The filtrate was then analysed photometrically for molybdenum as described in ref. 15 using a Cary Varian UV-Vis spectrometer. In a second experiment, another acetone filtrate was evaporated by heating in a glass beaker. A few milliliters of aqua regia were then added to the beaker and evaporated completely by heating. The aqua regia would dissolve any nanoparticles or NW fragments which could have passed through the filter membrane. After adding 2 molar hydrochloric acid, the solution was again analysed

photometrically for molybdenum. The detection limit for molybdenum is 5 ppm using this method.¹⁵ A JEOL 3000 F TEM equipped with an Oxford Instruments INCA detector operated at 300 kV was used for energy-dispersive X-ray spectroscopy (EDX) analysis of the sediments and solute in acetone and solute in NMP. The same microscope, which is also fitted with a Gatan imaging filter (GIF), was also used for the electron energy loss spectroscopy (EELS) characterisation.

3. Sedimentation

Due to the sonication applied to the solutions, even particles in the raw material that are insoluble in a solvent will be dispersed. When the dispersion is left for a week however, we expect insoluble particles with similar chemistry and aspect ratio, henceforth referred to as a phase, to sediment out with a unique time constant τ , such that the concentration at a time t follows the equation

$$C(t) = C_0 + \sum_n C_n e^{-t/\tau_n} \quad (1)$$

where C_0 is the concentration of material stably dissolved (at least within the time frame of the experiment), and C_n and τ_n are the initial concentration and sedimentation time constant of sediment n , respectively.⁵ This was monitored using the linear transmitted intensity I through the dispersion, which varies with $C(t)$ as given by the Lambert-Beer law:

$$I(t) = I_0 e^{-\alpha C(t)l} \quad (2)$$

$$C(t) = \frac{1}{\alpha l} \ln \left(\frac{I_0}{I(t)} \right) \quad (3)$$

However, while the path length l and the transmission of the pure solvent I_0 are constant, the absorption coefficient α is different for each phase in the dispersion. We therefore work in terms of the turbidity $T(t)$:

$$T(t) = \alpha C(t) = \frac{1}{l} \ln \left(\frac{I_0}{I(t)} \right) \quad (4)$$

which from eqn ((1)) follows

$$T(t) = T_0 + \sum_n T_n e^{-t/\tau_n} \quad (5)$$

The significance of these constants in relation to the sedimentation curve for NW material in IPA is shown in Fig. 1.

eqn ((5)) with $n = 1, 2$ or 3 was fitted to each sedimentation curve, and the number of sedimenting phases n determined from the quality of these fits (the sedimentation curves and fitting parameters for all solvents are given in the supplementary information). In almost all cases the best fit occurred for $n = 2$, that is for a fit that assumes 2 sedimenting phases and one soluble one. Acetone and THF were found to lead to three sedimenting phases, while BA only lead to one.

The most important parameters from these fits are T_0 , which gives an idea of how much material is retained by the solvent, and the final time constant, or purification time, which tells us how long it takes to reach this stage. These parameters are shown in Fig. 2 for all the solvents investigated. The best solvents for Mo₆S₂I₈ NW material are DMF, DMAc, CP, and NMP, with T_0/T_{initial} of 41, 37, 37 and 29%, respectively.

Fig. 1 Sedimentation curve for NW material in IPA.

DMF is the most useful of these, with a purification time of 8 h (vs. 50 h for DMAc, 62 h for CP, and 112 h for NMP).

It also is worth noting that IPA and acetone are relatively poor solvents, and that the NW material did not dissolve at all in water. Water, IPA and acetone were fairly good solvents for $\text{Mo}_6\text{S}_3\text{I}_6$ and $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ material, suggesting that $\text{Mo}_6\text{S}_2\text{I}_8$ NW material has a different surface chemistry to the other two stoichiometries.

Discussion of solvent quality thus far has been solely on the basis of the solute turbidity T_0 . This is problematic because if the solute is not formed by the same phase in each solvent, solute turbidity is not proportional to the amount of material retained. Furthermore, we are not interested in solvents where impurities or large NW bundles constitute the solute because the purpose of this study is to permit the isolation of thin NW bundles for further characterisation. The sedimenting phases and solute for each solvent were therefore characterised by TEM. Typical images of the phases from acetone and DMF are shown in Fig. 3.

It can be seen that in acetone, large NW bundles are the first to sediment out (a), followed by low aspect ratio bundles (b). The last two images provide another reason why it is helpful to complement the quantitative sedimentation study with

Fig. 3 Phases in acetone: thick NW bundles (a), low aspect ratio bundles (b), thin, tangled bundles (c), isolated thin bundles (d). Phases in DMF: thick NW bundles (e), low aspect ratio bundles and thick bundles (f), thin bundles (g).

qualitative TEM characterisation—acetone is one of the few solvents where sedimentation curve fitting predicts three sedimenting phases, yet the micrographs show that both this third sediment (c) and the solute (d) consist of thin NW bundles. This means that to obtain thin NW bundles in acetone, it is not necessary to wait for the final phase to sediment out unless unentangled thin bundles are required. This decreases the purification time from 57 h to 13 h, making acetone one of the fastest solvents.

The sediment and solute morphologies for all solvents are summarised in Table S11.† The sedimentation time constant τ can be shown to increase with aspect ratio of the relevant phase,⁵ so from a purely physical standpoint, the quasi-spherical impurities and bundles with a low aspect ratio should sediment out first, followed by thick bundles, leaving only thin ones in solution.

In most solvents, impurities, low aspect ratio bundles, and thick bundles do sediment out first, though not necessarily in that order, and thin NW bundles are always present in the solute. It is worth noting that impurities were only found in a few samples, suggesting that the raw material is actually quite pure, in contrast to raw $\text{Mo}_6\text{S}_3\text{I}_6$ or $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ material.^{4,5}

Nevertheless, some solvents like BA, CHCl_3 and GBL seem to stabilise impurities as they are found in the solute. IPA and toluene do not even appear to have distinct phases, but simply lose some of the material dispersed in them over time.

We attribute these disparities to chemical interactions between solvent and dispersate. There are too many variables

Fig. 2 Column chart showing the solute turbidity as a fraction of initial turbidity (red) and final sedimentation times (black) for all solvents investigated.

Table 1 Statistics on bundle diameter distributions

Concentration, $C_0/\text{mg l}^{-1}$	Number of measurements	Mean diameter/nm	Standard error/nm
1	218	11.2	1.6
0.5	255	10.5	0.8
0.1	135	6.59	0.8
0.05	100	8.58	0.7
0.01	5	6.41	2

involved to attempt to explain the behaviour of different solvents further—polarity, surface tension, and molecule size and shape are likely to all play a role—but empirically the TEM study helps us understand which solvents work best. CP and DMAc were among our best solvents, but as neither fully removes low aspect ratio NW bundles, and the former does not disentangle thin bundles, it would be unviable to use them for further experiments. Acetone on the other hand, while having a much lower yield, provides a quick way of isolating thin NW bundles, and if we are interested only in the impurities in the powder, CHCl_3 would be our solvent of choice. Fig. 2 and Table S11 (ESI)[†] provide an extremely useful empirical framework to tune the NW bundle shape to what is required for further experiments or practical applications.

In most cases however it is expected that a high concentration of thin NW bundles only will be desired, which are only obtained in DMF and NMP. This process takes 14 times longer in NMP than in DMF so more detailed investigations into NW solutions were carried out in DMF only. The morphology of the different phases in DMF is also shown in Fig. 3. Thick NW bundles again form the first sedimenting phase (e), though they are now also present in the second one (f), along with low aspect ratio NW bundles. This makes DMF less suitable for separating out these low aspect ratio bundles than acetone for example. However it is equally good at isolating thin nanowire bundles in the solute (g), and retains much larger quantities.

4. Surface energy

Although the solvent study was so far largely empirical, it is possible to extract from it the approximate surface energy of $\text{Mo}_6\text{S}_2\text{I}_8$ NWs using a method that has already been successfully applied to CNTs and graphene.^{16–18} It considers the energy changes that occur upon solvation. The free energy of mixing is given by the well-known formula

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (6)$$

and must be negative for solvation to occur, giving

$$\Delta H_{\text{mix}} < T\Delta S_{\text{mix}}. \quad (7)$$

The configurational entropy for a NW solution is very low because NWs are highly ordered structures, and the overall entropy for one-dimensional nanostructures can be shown to be very low from a consideration of Flory's equations.¹⁶ For solvation to be possible at modest temperatures it is therefore necessary to minimise the enthalpy of mixing. Consideration of the energy changes that occur when NWs are brought from

infinity into voids in the solvent gives the following expression for the enthalpy of mixing¹⁶

$$\frac{\Delta H_{\text{mix}}}{V_{\text{mix}}} = \frac{4}{d}(\sqrt{\gamma_{\text{nanowire}} - \gamma_{\text{solvent}}})^2 \phi \quad (8)$$

where V_{mix} is the volume of the mixture, d is the NW bundle diameter, ϕ is the NW volume fraction, and γ_i is the surface energy of i . According to this equation it is impossible to obtain a negative enthalpy of mixing for a NW-solvent system, but it can be minimised by matching NW and solvent surface energies, *i.e.* for

$$\gamma_{\text{nanowire}} = \gamma_{\text{solvent}} \quad (9)$$

The solubility of NWs will therefore be highest in a solvent that has the same surface energy as the NWs. Fig. 4 shows a plot of NW solute turbidity T_0 for each solvent against solvent surface energy. T_0 values are those presented previously for $\text{Mo}_6\text{S}_2\text{I}_8$ (Fig. 4a), and taken from the literature for $\text{Mo}_6\text{S}_3\text{I}_6$ (Fig. 4b) and $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ ^{4,5} (Fig. 4c). Solvent surface tensions from the literature^{17,19,20} were converted to surface energies at 297 K using a constant solvent surface entropy of $0.1 \text{ mJ m}^{-2} \text{ K}^{-1}$,¹⁶ and the surface form of eqn ((6)),

$$\gamma = \tau + T\Delta S \quad (10)$$

where γ is surface energy (enthalpy), and τ is the surface tension (Gibbs free energy).

It shows that all the best solvents for $\text{Mo}_6\text{S}_2\text{I}_8$ do indeed have similar surface energies, while none of the solvents with a surface energy outside the $65\text{--}77 \text{ mJ m}^{-2}$ window (shaded in Fig. 4a) worked very well. We deduce that the surface energy of $\text{Mo}_6\text{S}_2\text{I}_8$ NWs is approximately that of the best solvent, DMF, but due to the discontinuous nature of the data could lie anywhere between the surface energies of the solvents closest in surface energy to DMF, DMAc and BA, giving

$$\gamma_{\text{Mo}_6\text{S}_2\text{I}_8\text{nanowire}} = 67 \pm 2 \text{ mJ m}^{-2} \quad (11)$$

From similar plots for $\text{Mo}_6\text{S}_3\text{I}_6$ and $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ also shown in Fig. 4b and c, respectively, it is immediately clear that $\text{Mo}_6\text{S}_2\text{I}_8$ NWs must have a higher surface energy than the other two stoichiometries. This is not surprising as we had already observed that these NW stoichiometries dissolve well in different solvents, and our determination of surface energies stems from solubility plots.

However the fact that the surface energy windows for good solvents hardly overlap means there must be significant differences in the atomic structures of $\text{Mo}_6\text{S}_2\text{I}_8$ NWs and the previously investigated stoichiometries, in particular in the occupancy of sites on the NW surface, and high-angle annular dark field scanning transmission electron microscopy coupled

Fig. 4 T_0 vs. surface energy plots for all three Mo–S–I NW stoichiometries. Shaded areas indicate surface tensions of good NW solvents. DMSO is excluded for $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ because it does not retain NWs but a lot of impurities.

with structural and image modelling is underway to fully determine the structure of $\text{Mo}_6\text{S}_2\text{I}_8$ NWs.

Unfortunately, we cannot reliably quantify the surface energy of the other NW stoichiometries because there is no clear peak in T_0 . However this in itself suggests that the $\text{Mo}_6\text{S}_2\text{I}_8$ solute is more chemically homogeneous. The raw material also appears to be more pure because the maximum T_0 for $\text{Mo}_6\text{S}_2\text{I}_8$ is 42%, as compared to 20% for $\text{Mo}_6\text{S}_3\text{I}_6$ and 33% for $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$. This idea is reinforced by the fact that fewer non-nanowire impurities were seen in TEM images of $\text{Mo}_6\text{S}_2\text{I}_8$ compared to the other two stoichiometries (see Table S11 in the ESI†).^{4,5} In fact, the ‘poor’ T_0 for $\text{Mo}_6\text{S}_2\text{I}_8$ in acetone is better than the ‘good’ one for $\text{Mo}_6\text{S}_3\text{I}_6$. In comparison to other stoichiometries therefore, there seems to be little disadvantage to processing $\text{Mo}_6\text{S}_2\text{I}_8$ in weaker, but more volatile solvents. Nevertheless these data must be treated with caution because $T_0 = \alpha_0 C_0$, and α_0 at the wavelength used for sedimentation (650 nm) is not known for all stoichiometries.

5. UV-vis-NIR spectroscopy and photometric analysis

The optical absorption behaviour of $\text{Mo}_6\text{S}_2\text{I}_8$ was compared to the $\text{Mo}_6\text{S}_3\text{I}_6$ and $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ materials previously characterised.^{4,5} A full comparison of all the separated phases

of all the three different stoichiometries is presented in Fig. 5. Firstly, all spectra, except that for the first sediment from $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ which contains mainly chemical impurities,⁵ exhibit peaks at 1.8 and 2.8 eV. These are attributable to NWs in all cases, and indicate some elements of the NW structure or chemistry are common to all three stoichiometries. However, the two UV peaks at 3.5 and 4.4 eV occur only in $\text{Mo}_6\text{S}_2\text{I}_8$. There is a peak for both of the other compositions that, like this UV peak, becomes stronger with decreasing concentration, but that is in the infrared, at 0.65 eV. $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ solute also has another such peak at 0.85 eV. Assuming as before that peaks that become more prominent with decreasing concentration stem from thin bundles or individual wires, this means that some bond energies or electronic transitions are of higher energy in $\text{Mo}_6\text{S}_2\text{I}_8$ than in NWs of the other compositions. This also concurs with the higher surface energy deduced earlier. The optical absorption coefficient α_0 of thin $\text{Mo}_6\text{S}_2\text{I}_8$ NWs was calculated, from plots of turbidity against concentration for the solute in DMF, using eqn (4), as 8.0×10^2 , 4.9×10^2 and $5.6 \times 10^2 \text{ m}^2 \text{ kg}^{-1} \pm 2 \times 10^2$ at a wavelength of 450, 650, 700 nm, respectively.

Photometric analysis for molybdenum, performed as described in the Experimental method section, showed that a dispersion of the NW material in acetone contained neither detectable amounts of molecular molybdenum species nor nanoparticles which could have passed through a 0.2 μm pore size filter membrane. This strongly illustrates the mechanical and chemical stability of the NW dispersions.

6. Debundling

Having examined the behaviour of $\text{Mo}_6\text{S}_2\text{I}_8$ NWs in different solvents we now turn our attention to what happens to the bundle sizes upon dilution of solutions of thin NW bundles. A clearly discernible trend would permit tuning of bundle size to that required for a specific application simply by adjusting the concentration, which would greatly facilitate processing. Such trends have been observed for carbon nanotubes and other Mo–S–I NWs, so the same behaviour is anticipated here.^{5,6,21}

Bundle lengths are not expected to change much because bundles are unlikely to rupture on dilution, and measuring them is extremely time-consuming because bundles are rarely straight. Research here is therefore confined to bundle diameters, which change relatively easily, as is evidenced by Fig. 6 which shows the extremely frayed end of a large NW bundle.

The ease with which bundles fray actually introduces another difficulty because many bundles split into branches, and few bundles have the same diameter all the way along their length. To overcome this, the diameter of each bundle was measured in several locations and average taken. The bundle diameter distributions thus measured by tapping mode AFM for different dilutions of the solute (originally at concentration C_0) in DMF and the sample images are both shown in the online supplementary. Measurements of the bundle height, rather than of the bundle width, were used to minimise the effect of the AFM tip shape on the results.

Debundling clearly takes place because the larger bundles observed at higher concentrations are no longer observed at

Fig. 5 UV-vis-NIR spectra of sediments and solute of $\text{Mo}_6\text{S}_2\text{I}_8$ (top), $\text{Mo}_6\text{S}_3\text{I}_6$ (middle) and $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ (bottom) NWs.

lower concentrations, and the only explanation is that they debundle into bundles of lower diameter. However it is difficult to discern a shift in the distribution at low diameters

Fig. 6 Fraying NW bundle.

by eye, so statistics on these distributions are presented in Table 1.

It can be seen that the mean diameter decreases with decreasing concentration. The $0.05 C_0$ sample is the only anomaly to this, and with standard errors amounting to 10% of the values considered is not a far outlier. It can also be seen why the experiment was not continued to higher dilutions—it proved very difficult to find any NWs in samples prepared from a $0.01 C_0$ solution.

Debundling has also been observed in solutions of the other Mo–S–I NW stoichiometries^{5,6} as well as carbon nanotubes,²⁰ and can be explained as follows. Debundling of NW bundles creates a higher number of bundles, raising the configurational entropy of the system. It is therefore a thermodynamically viable process. However if the number of bundles becomes so high that they are likely to collide while tumbling through the solvent, they are likely to reaggregate. A dynamic equilibrium will therefore be reached at a certain number of bundles per unit volume which is such that each bundle only just occupies its own volume of solvent. This volume depends on the length of the bundles, not on their diameter, and is therefore approximately constant over the debundling process. This means the number of bundles per unit volume will also be constant. It is given simply by the (mass) concentration of NWs divided by the mass of a NW:

$$\frac{N_{\text{bundles}}}{V_{\text{solution}}} = \frac{4C_{\text{NW}}}{\rho\pi\bar{d}^2l} \quad (12)$$

ρ is the density of NWs, l their length and $\bar{d}$ their mean diameter. Assuming as we did before that the bundle length is constant, we get

$$\bar{d} = A\sqrt{C_{\text{NW}}}, \text{ where} \quad (13)$$

$$A = \sqrt{\frac{4}{\rho\pi l \left(\frac{N_{\text{bundles}}}{V_{\text{solution}}}\right)}} \quad (14)$$

To determine how well this model fits our data, a plot of $\bar{d}$ as a function of C_{NW} is shown in Fig. 7:

The fit corresponding to the model as it stands is given by the dashed line. It can be seen that this fit is not very good, making it necessary to modify the model to explain the debundling of these NWs. We do this by suggesting that debundling occurs for the reasons detailed in the original model, but does not occur indefinitely, *i.e.* that there are not just isolated NWs as we approach infinite dilution, but bundles of a finite mean diameter d_0 . While configurational entropy will continually drive the system to debundle, if the enthalpy change associated with debundling is greater than $T\Delta S$, ΔG for debundling will be positive and it will therefore cease to occur. Such an enthalpy increase can arise from the additional NW surfaces that are created upon debundling, and we found previously that $\text{Mo}_6\text{S}_2\text{I}_8$ NWs have a much higher surface energy than the other Mo–S–I NWs. We therefore propose an extension to the original model to include a constant d_0 , the mean bundle diameter at infinite dilution, such that

$$\bar{d} = d_0 + A\sqrt{C_{\text{NW}}}. \quad (15)$$

Fig. 7 Mean bundle diameter vs. solute concentration. Dashed line shows $d = A \times C^{1/2}$ fit. Solid line shows $d = d_0 + A \times C^{1/2}$ fit.

The fit corresponding to this model is given by the solid line in Fig. 8. This fit is much better than the original one, suggesting that $\text{Mo}_6\text{S}_2\text{I}_8$ NWs, in contrast to $\text{Mo}_6\text{S}_3\text{I}_6$ and $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ NWs,^{5,6} do not debundle fully — the fit returns $d_0 = 6.4$ nm, while the diameter of individual NWs is about 1 nm.²² This has important practical implications because while there are doubtless some individual NWs at lower concentrations, as

Fig. 8 Variation of sulfur (a) and Iodine (b) content with an estimated bundle diameter. Horizontal lines correspond to nominal stoichiometry ($S = 2$, $I = 8$). Inset in sulfur plot: variation of difference between standardless analysis and analysis with standards, with estimated bundle diameter.

shown in the histograms in the SI,[†] only a small fraction of these can ever be attained by dilution because the equilibrium bundle diameter is never below 6.4 nm.

7. Absolute concentration of solute

The easiest way to find the absolute concentration C_0 is to use eqn ((3)), as we now know T_0 from the sedimentation experiments and α_0 from the UV-vis spectroscopy. This gives $0.04 \text{ g l}^{-1} \pm 0.02$ of solute, or $50 \pm 15 \text{ wt\%}$. This is roughly what we had expected from turbidity measurements anyway ($T_0 = 41\%$), suggesting that the optical absorption coefficients of the different phases are similar.

C_0 was also found by isolating the solute from a 0.08 g l^{-1} dispersion in DMF, centrifuging, allowing the solvent to evaporate and weighing it to find the percentage of material retained (see the experimental methods for details). Applying this method 47% of the nanowire powder was successfully retrieved. This agrees with the 50 wt% derived from optical measurements within experimental error. The same separation method was applied to higher concentration dispersions in order to find out if the percentage of material retained was varying with the initial concentration. A starting concentration of 5 g l^{-1} allowed 66 wt% of the material to be retrieved after centrifugation; while for a dispersion at an initial concentration of 0.8 g l^{-1} 54 wt% was successfully recovered. Therefore on average, $57 \pm 10 \text{ wt\%}$ of the starting material was retained by the solvent. More importantly, this confirms that much more solute can be retained from $\text{Mo}_6\text{S}_2\text{I}_8$ than from other Mo–S–I NWs, where C_0 never exceeds 12 wt%.^{4,5} Perhaps even more crucially, the absolute C_0 from the 5 g l^{-1} dispersion is 3300 mg l^{-1} , an order of magnitude higher than the greatest attained C_0 values of 340 mg l^{-1} for $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$,⁵ 60 mg l^{-1} for $\text{Mo}_6\text{S}_3\text{I}_6$,⁴ and 20 mg l^{-1} for CNTs.²⁰

8. Stoichiometry determination by EELS and EDX

Much of the experimental evidence presented so far suggests that the structure of $\text{Mo}_6\text{S}_2\text{I}_8$ NWs will be significantly different to that of $\text{Mo}_6\text{S}_3\text{I}_6$ and $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ NWs. However before the structure can be found, the stoichiometry needs to be checked. The $\text{Mo}_6\text{S}_2\text{I}_8$ formula is only representative of the composition of the starting material used to make them, and while for the other stoichiometries starting and end compositions were the same, this is not a given. Chemical analysis was carried out on all the phases separated in acetone using both EELS and EDX detectors in a TEM to ensure that the acquired spectrum came from one NW or particle only. The use of EELS to identify the stoichiometry of the NWs proved to be rather difficult. A typical EELS spectrum of the purified $\text{Mo}_6\text{S}_2\text{I}_8$ NWs is shown in the ESI.[†] The sulfur $L_{2,3}$ -edge appears delayed, starting about 165 eV and peaking around 200 eV, while the L_1 edge appears at 225 eV. The molybdenum $M_{4,5}$ -edge starts instead at around 227 eV and peaks about 300 eV, overlapping with the sulfur edge. It was not easy to use a standard to subtract the sulfur edge from underneath the molybdenum edge as the structure on the sulfur edge changes significantly with bonding environment. In the case of the

NWs, the sulfur edge is fairly featureless, meaning that it may be possible to fit a background just before the Mo edge. It is likely that the shape of the edge will differ from the usual background model and so an error may be introduced by this method. Another approach would be to use the Mo $M_{2,3}$ -edge rather than the $M_{4,5}$ -edge. These edges appear as white lines at ~ 400 eV (see spectrum in the ESI).[†] The difficulty with using these edges for quantification is the cross-section, as it is the $M_{4,5}$ cross section which tends to be tabulated. All these reasons led us to prefer EDX over EELS for a more accurate stoichiometric characterisation of the NWs.

Another problem had to be resolved in the EDX characterisation, because the Mo $L\alpha$ and S $K\alpha$ peaks are only 40 eV apart, and the energy resolution of EDX is around 150 eV.^{23,24} Peak subtraction was therefore necessary, and two different approaches were used to check consistency: standardless analysis, which relies on scattering cross-sections from the INCA software; and analysis with standards. MoO_3 and MoS_2 standards were used to obtain the Mo $K\alpha$:Mo $L\alpha$ ratio and the Mo:S k-factor, respectively. The I $L\alpha$ peak was only analysed using the software because no standard containing iodine and molybdenum or sulfur was available. The mean results for the NWs, averaged over 61 bundles, are shown in Table 2.

Fixing the molybdenum concentration at 6 atoms per formula unit, which makes sense because molybdenum forms octahedral Mo_6 clusters in many materials including other Mo–S–I NWs, we get the formula $Mo_6S_{2.6}I_{8.8}$ from the automated analysis, and $Mo_6S_{2.3}I_{8.8}$ using the Mo:S ratio obtained from manual analysis. EDX is generally only considered to be accurate to $\pm 6\%$ at most²³ and is potentially much worse, particularly in standardless analysis, so this data can be taken to confirm the original stoichiometry. However, it also means a mixture of $Mo_6S_2I_8$ and $Mo_6S_3I_6$ is just as likely. The diameters of NW bundles on which EDX was carried out were estimated to determine whether the bundle composition changed with bundle size. Such a trend could suggest intercalation of the bundles with excess Mo, S or I. Plots of sulfur and iodine content against estimated bundle diameter are shown in Fig. 8.

No clear trend is discernible for the sulfur content, though the difference in the values returned by the two analysis routes (inset in Fig. 8a) decreases with increasing bundle diameter, which can be attributed to the higher number of counts in the detector and the associated improvement in the signal-to-noise ratio. The negative sulfur concentrations are artefacts arising from a low number of counts and the collective analysis of all spectra, and were not included in the mean composition shown earlier.

The iodine content (Fig. 8b) on the other hand appears to rise with bundle diameter. This can be attributed to electron-beam induced iodine desorption, which has also been observed

Table 2 NW composition from EDX

	Standardless			With standards	
	Mo_6	S_y	I_z	y	z
Mean standard error		2.6	8.8		2.3
		0.14	0.21		0.15

Table 3 Composition of the impurity particles

Mo6	S_y	I_z	S:Mo ratio	Mo_6S_y	% difference
	y	z		y	
	6.6	2.4	1.08	6.46	2%
	6.9	2.3	1.08	6.46	7%
	3.88	9.88	0.45	2.67	31%

by other groups attempting chemical analysis of Mo–S–I NWs,²⁵ and was particularly significant here as EDX was carried out at 300 kV. It is stronger for small bundles because the beam had to be condensed more to ensure a sufficiently high X-ray yield. Another reason is that washing in acetone may not have removed all the excess iodine originally present in the raw nanowire material. Excess iodine is more likely to remain entrapped in a bundle despite exposure to acetone if the bundle is thicker, because the acetone cannot penetrate through the bundle. While bundle-by-bundle chemical analysis is informative, it would be helpful if the material could be analysed using a bulk technique such as XPS. Impurities present in the sediments in acetone were also analysed to determine how large an effect they were likely to have on the result of a bulk measurement on the as-synthesised NW powder.

The compositions of 3 different impurity particles are given in Table 3.

The first two appear to be $Mo_6S_6I_2$ Chevrel phase particles, while the last one may in fact be a NW bundle of some composition containing excess iodine. The compositions of these impurities illustrate the importance of an *in situ* analytical technique such as EDX to determine the composition of NW bundle by examining NW bundles only.

9. Conclusion

We have demonstrated that $Mo_6S_2I_8$ NWs, like $Mo_6S_3I_6$ and $Mo_6S_{4.5}I_{4.5}$ NWs, can be purified by dispersion in solvents. However unlike those NWs, they only dissolve well in extremely non-volatile, hygroscopic solvents like DMF, which retains 57 wt% raw material in the form of thin NW bundles. While this makes processing much more difficult because it is difficult to remove the solvent once the nanowires have been purified, the attainable yield is much greater than in any similar system, with 3.3 g l^{−1} solutions of thin nanowire bundles having been attained in DMF. It is also possible to process NWs using other solvents, and the sedimentation study and TEM characterisation provide an invaluable empirical framework to select the solvent for a given purpose. For example, these NWs can be purified using more volatile solvents such as acetone or ethanol. There is less material (17 and 18% by turbidity respectively), but it is easier to purify, the solvent is cheaper, and unless a solubility limit not seen in DMF arises in these solvents, solutions in excess of 1 g l^{−1} should be attainable in them. It is merely water which is absolutely incapable of dispersing $Mo_6S_2I_8$ NWs.

The surface energy of the NWs at 297 K was determined from their solubility in different solvents to be 67 mJ m^{−2}, more than for $Mo_6S_3I_6$ and $Mo_6S_{4.5}I_{4.5}$ NWs. Like the UV peaks found in the UV-vis-NIR spectrum of thin $Mo_6S_2I_8$ NW

bundles, this suggests stronger bonding, and a differing chemistry of $\text{Mo}_6\text{S}_2\text{I}_8$ NWs. The mean composition of these NWs is $\text{Mo}_6\text{S}_{2.3}\text{I}_{8.8}$ as determined by EDX, which within experimental error means the real composition could be $\text{Mo}_6\text{S}_2\text{I}_8$ as expected, or a mixture of $\text{Mo}_6\text{S}_2\text{I}_8$ and $\text{Mo}_6\text{S}_3\text{I}_6$ NWs. EDX measurements on impurities confirmed the importance of analysing individual, or at least purified NWs, rather than the raw material as a whole. Difficulties related to the overlapping and delayed start of the sulfur and molybdenum edges has proved electron energy loss spectroscopy (EELS) to be inefficient in determining the composition of these materials.

Another processing obstacle is that AFM measurements showed that $\text{Mo}_6\text{S}_2\text{I}_8$ NWs never fully debundle. While this makes it viable to work at the high concentrations that have been shown to be attainable because the decrease in mean diameter with concentration is of little benefit, it does not provide a route to obtain a high yield of individual NWs. This will restrict the viability of applications for single $\text{Mo}_6\text{S}_2\text{I}_8$ NWs. However the reason for their drawbacks is perhaps their greatest strength — the fact that they are chemically different to $\text{Mo}_6\text{S}_3\text{I}_6$ and $\text{Mo}_6\text{S}_{4.5}\text{I}_{4.5}$ NWs, while cumbersome, promises to provide a greater diversity of properties in the Mo–S–I NW system. There is particular potential for novel electronic properties of $\text{Mo}_6\text{S}_2\text{I}_8$ NWs as these are very sensitive to atomic structure.

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References

- 1 D. Vrbanic, M. Remškar, A. Jesih, A. Mrzel, P. Umek, M. Ponikvar, B. Jančar, A. Meden, B. Novosel, S. Pejovnik, P. Venturini, J. C. Coleman and Dragan Mihailović, *Nanotechnology*, 2004, **15**, 635–638.
- 2 European Patent, EP1541528, EP20030028188, 2005.
- 3 D. Mihailovic, *Prog. Mater. Sci.*, 2009, **54**, 309–350.
- 4 D. McCarthy, V. Nicolosi, D. Vengust, D. Mihailovic, G. Compagnini, W. J. Blau and J. N. Coleman, *J. Appl. Phys.*, 2007, **101**, 014317–014317.
- 5 V. Nicolosi, D. Vrbanic, A. Mrzel, J. McCauley, S. O'Flaherty, D. Mihailovic, W. J. Blau and J. N. Coleman, *J. Phys. Chem. B*, 2005, **109**, 7124–7133.
- 6 V. Nicolosi, D. Vengust, D. Mihailovic, W. J. Blau and J. N. Coleman, *Chem. Phys. Lett.*, 2006, **425**, 89–93.
- 7 A. Kis, G. Csanyi, D. Vrbanic, A. Mrzel, D. Mihailovic, A. Kulik and L. Forró, *Small*, 2007, **3**, 1544.
- 8 R. Murphy, Valeria Nicolosi, Y. Hernandez, D. McCarthy, D. Richard, D. Vrbanic, A. Mrzel, D. Mihailovic, W. J. Blau and Jonathan N. Coleman, *Scr. Mater.*, 2006, **54**, 417–420.
- 9 M. Uplaznik, B. Bercic, J. Strle, M. I. Ploscaru, D. Dvorsek, P. Kušar, M. Devetak, D. Vengust, B. Podobnik and D. Mihailovic, *Nanotechnology*, 2006, **17**, 5142–5146.
- 10 J. Strle, D. Vengust, M. Ploscaru, M. Uplaznik and D. Mihailovic, *Phys. Status Solidi B*, 2008, **245**, 2115–2119.
- 11 M. Žumer, V. Nemanič, B. Zajec, M. Remškar, M. Ploscaru, D. Vengust, A. Mrzel and D. Mihailović, *Nanotechnology*, 2005, **16**, 1619–1622.
- 12 L. Joly-Pottuz, F. Dassenoy, J. M. Martin, D. Vrbanic, A. Mrzel, D. Mihailovic, W. Vogel and G. Montagnac, *Tribol. Lett.*, 2005, **18**, 385–393.
- 13 C. Perrin and M. Sergent, *J. Chem. Res. Synopses*, 1983, 38–39.
- 14 V. Nicolosi, D. Vrbanic, A. Mrzel, J. McCauley, S. O'Flaherty, D. Mihailovic, W. J. Blau and J. N. Coleman, *Chem. Phys. Lett.*, 2005, **401**, 13–18.
- 15 E. Roscoe and R. V. Olson, *Anal. Chem.*, 1950, **22**, 328–330.
- 16 S. Park, J. An, I. Jung, R. D. Piner, S. J. An, X. Li, A. Velamakanni and R. S. Ruoff, *Nano Lett.*, 2009, **9**, 1593–1597.
- 17 S. D. Bergin, V. Nicolosi, P. V. Streich, S. Giordani, Z. Sun, A. H. Windle, P. Ryan, N. P. P. Niraj, Z. T. Wang, L. Carpenter, W. J. Blau, J. J. Boland, J. P. Hamilton and J. N. Coleman, *Adv. Mater.*, 2008, **20**, 1876–1881.
- 18 Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari and J. N. Coleman, *Nat. Nanotechnol.*, 2008, **3**, 563–568.
- 19 *Knovel Critical Tables, Basic Physical Properties of Common Solvents*, 2nd edn, 2003, 385.
- 20 Surface tension values of some common test liquids for surface energy analysis. at <http://www.surface-tension.de/>.
- 21 S. Giordani, S. D. Bergin, V. Nicolosi, S. Lebedkin, M. M. Kappes, W. J. Blau and J. N. Coleman, *J. Phys. Chem. B*, 2006, **110**, 15708–15718.
- 22 V. Nicolosi, P. D. Nellist, S. Sanvito, E. C. Cosgriff, S. Krishnamurthy, W. J. Blau, M. L. H. Green, D. Vengust, D. Dvorsek, D. Mihailovic, G. Compagnini, J. Sloan, V. Stolojan, J. D. Carey, S. J. Pennycook and J. N. Coleman, *Adv. Mater.*, 2007, **19**, 543–547.
- 23 D. C. Joy, A. D. Romig and J. Goldstein, *Principles Anal. Electron Microsc.*, 1986, 448.
- 24 P. J. Goodhew, F. J. Humphreys and R. Beanland, *Electron Microsc. Anal.*, 2001, 251.
- 25 D. Mandrino, D. Vrbanic, M. Jenko, D. Mihailovic and S. Pejovnik, *Surf. Interface Anal.*, 2008, 40.