

Thio sol–gel synthesis of titanium disulfide from titanium thiolates

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Titanium disulfide, TiS_2 , has been successfully prepared *via* a thio ‘sol–gel’ process using titanium(IV) thiolate precursors as the metal source. Four precursors have been investigated, namely $[\text{Ti}(\text{SBU}^t)_4]$, $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_9]$, $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ and $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_3][\text{SC}_6\text{F}_5]_2$. The titanium(IV) thiolate reacts at room temperature with H_2S to form a precipitate which upon annealing at 800°C under H_2S results in the formation of crystalline TiS_2 . The TiS_2 produced was analysed by powder X-ray diffraction, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA) and Raman spectroscopy. Annealing the precipitate obtained from the thio ‘sol–gel’ process at 600°C under H_2S results in the formation of a mixture of crystalline TiS_2 and $\text{Ti}_{1.25}\text{S}_2$.

Introduction

Transition metal dichalcogenide compounds are an important class of materials that exhibit a wide range of electronic and optical properties.^{1,2} These materials are suitable for use as solid lubricants and hydrogenation catalysts.^{3,4} In the particular case of titanium disulfide (TiS_2), it is used in high-energy density batteries where lithium is intercalated between the layers of the TiS_2 lattice.⁵ However, the properties of TiS_2 can be affected by inhomogeneities and impurities in the material which may be a result of the preparation process.^{1,2} The conventional synthesis of TiS_2 involves a high temperature solid-state reaction between the component elements.⁶ This process typically takes place over a period of days, with intermediate additions and grinding, and involves temperatures over 1000°C . As well as being energy consuming, this method can result in high levels of impurities being incorporated into the product. There are a number of other procedures available for preparing thin films of TiS_2 including sputtering,⁷ evaporation⁸ and plasma-assisted chemical vapour deposition (CVD).⁹ In addition, TiS_2 thin films have been prepared *via* thermal CVD reactions of TiCl_4 with H_2S or other sulfur sources, including *tert*-butylthiol and bis(trimethylsilyl) sulfide.^{10,11} More recently, the CVD of a single source precursor $[\text{Ti}(\text{SBU}^t)_4]$ was reported to result in the formation of amorphous films of TiS_2 at 110 – 350°C .⁴

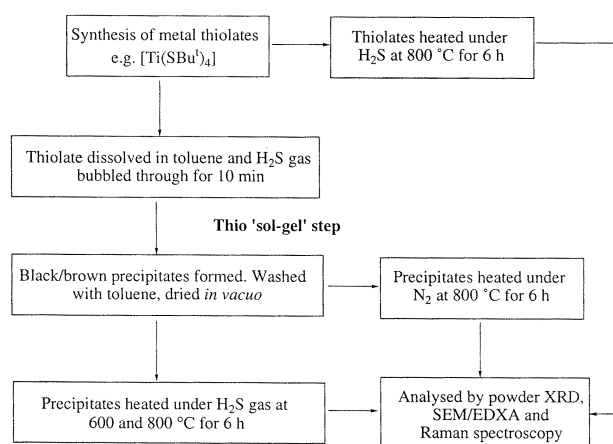
The use of metal alkoxides as precursors for the formation of metal oxides using sol–gel techniques has received significant attention for many years.¹² The preparation of oxide materials using sol–gel processes generally involves hydrolysis/condensation reactions of a variety of precursors (*e.g.* alkoxides) which limits its use in the formation of non-oxide materials.¹³ However, a thio ‘sol–gel’ type of process has been reported recently for the synthesis of TiS_2 involving the reaction of titanium alkoxides [*e.g.* $\text{Ti}(\text{OPr}^i)_4$] with H_2S gas in solution (*e.g.* toluene).^{13–15} A precipitate is obtained following a thiolysis/condensation reaction similar to the hydrolysis/condensation reactions involved in sol–gel processes.¹⁶ The precipitate, which is thought to be an alkoxysulfide, can be converted to TiS_2 by annealing it in flowing H_2S at 800°C . However, heat treatment of this precipitate at lower temperatures (600°C) results in the formation of a mixture of TiS_2 and TiO_2 .¹⁴

In this paper, we present the synthesis of TiS_2 using a modified thio ‘sol–gel’ process involving the reaction of titanium thiolates with H_2S in toluene. A thio ‘sol–gel’ process

of this type would be expected to provide a homogeneous product with a low level of impurities, *e.g.* oxygen, and to lower the temperature at which crystalline TiS_2 can be obtained. We have previously reported the synthesis and structural characterisation of a number of titanium thiolates including $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_9]$,¹⁷ $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$,¹⁸ and $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_3][\text{SC}_6\text{F}_5]_2$.¹⁸ Thio ‘sol–gel’ reactions were carried out using the aforementioned titanium thiolates and the previously reported compound $[\text{Ti}(\text{SBU}^t)_4]$ ^{4,19} as the metal source. The influence of temperature, H_2S and the thio ‘sol–gel’ step on the material obtained is discussed.

Experimental

The reactions of a range of titanium thiolates with H_2S were studied under a variety of conditions. The flow chart in Scheme 1 describes the different steps involved in the routes examined to prepare TiS_2 and these are described in detail below. All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. Owing to the toxic nature of H_2S all of the experiments were carried out in a well ventilated fume cupboard. All solvents were distilled from appropriate drying agents prior to use (sodium–toluene, THF and hexanes; CaH_2 for CH_2Cl_2). $[\text{Ti}(\text{SBU}^t)_4]$ was prepared using literature methods⁴ and the thiolates $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_9]$,



Scheme 1

$[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ and $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2$ were synthesised as described previously.^{17,18} All other reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London.

Physical measurements

¹H NMR spectra were recorded on Bruker AMX300 or DRX500 spectrometers. The NMR spectra are referenced to CD₂Cl₂ which was degassed and dried over molecular sieves prior to use; ¹H chemical shifts are reported relative to SiMe₄ (0.00 ppm). Thermolysis studies were performed in a Carbolite tube furnace. Raman spectra were run on a Renishaw system 1000 spectrometer with a notch filter using an excitation line wavelength of 632.8 nm from a HeNe laser. Spectra were calibrated against neon emission lines. Powder XRD measurements were recorded on a Siemens D5000 transmission diffractometer using germanium monochromated Cu-Kα₁ radiation (λ = 1.5406) as thin films. SEM profiles and EDXA were performed on a Hitachi S570 and FTIR spectra were recorded on a Nicolet 205 instrument.

Thio 'sol-gel' reactions of titanium thiolates with H₂S

Thio 'sol-gel' reactions were carried out using the titanium thiolates $[\text{Ti}(\text{SBu}^t)_4]$, $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$, $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ and $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2$ as the metal source. In a typical experiment, a sample of one of the aforementioned thiolates (0.300 g) was dissolved in toluene (40 cm³) to give a dark red solution. H₂S gas was bubbled through the solution at room temperature and a black precipitate formed immediately. The H₂S gas was allowed to bubble through the mixture for 10 min, after which the black solid was allowed to settle. The solvent was removed by syringe and the residue was washed twice with 20 cm³ of fresh toluene. The solid was dried *in vacuo* (10⁻³ mmHg) for 2 h resulting in a black/brown precipitate which was analysed by powder XRD and elemental analysis (Table 1). The black/brown precipitates were annealed in two different ways, under H₂S or under N₂, the details of which are described below for a typical experiment.

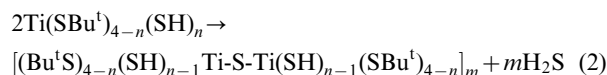
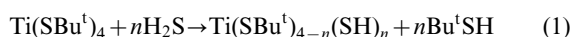
Annealing the precipitate under H₂S. A sample of the precipitate was placed in a ceramic boat and heated under a constant stream of H₂S gas at 800 °C for 6 hours using a furnace. A black solid resulted (black with a gold surface formed from the precipitate obtained from $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$) which was reanalysed by powder XRD, EDXA/SEM and Raman spectroscopy. The precipitate obtained from $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2$ was also annealed under H₂S at a temperature of 600 °C for 6 hours. Powder XRD and EDAX/SEM results were obtained on the resulting black solid.

Annealing the precipitate under N₂ (no H₂S present). A sample of the precipitate was placed in a ceramic boat and heated under a constant stream of N₂ at 800 °C for 6 hours using a furnace. A black solid resulted which was reanalysed by powder XRD, and EDXA/SEM.

Reaction of the titanium thiolates with H₂S (no thio 'sol-gel' step). To investigate the influence of the thio 'sol-gel' step, the thiolate precursors, $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$ and $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$, were annealed under H₂S without forming the initial precipitate (Scheme 1). In a typical experiment, a sample of the thiolate (0.30 g) was placed in a ceramic boat which was placed in a quartz tube. The thiolate was heated under a constant stream of H₂S gas at 800 °C for 6 hours using a furnace. A black solid resulted (black with a gold surface formed from the precipitate obtained from $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$) which was analysed by powder XRD, EDXA/SEM and Raman spectroscopy.

Results and discussion

Initial attempts to prepare TiS₂ involved the thio 'sol-gel' reaction of titanium thiolates with H₂S in toluene at room temperature. Four titanium thiolates were investigated as precursors, namely $[\text{Ti}(\text{SBu}^t)_4]$,⁴ $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$,¹⁷ $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ ¹⁸ and $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2$.¹⁸ In all cases, a black/brown precipitate formed immediately when H₂S was bubbled through the toluene solution of the thiolate. After work up, a ¹H NMR spectrum of the toluene washings showed the presence of R₂S₂ (R = Bu^t, CH₂Ph) when the thiolates $[\text{Ti}(\text{SBu}^t)_4]$ and $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$ were used. In contrast, the presence of $[\text{Et}_2\text{NH}_2][\text{C}_6\text{F}_5\text{S}]$ was detected in the washings from $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2$ and $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$. This suggests that the -SR ligands are replaced to some extent by -SH groups from H₂S during the thio 'sol-gel' reaction. Thus, the attack of the thiolate groups by H₂S forms the basis of the modified thio 'sol-gel' reaction investigated herein. This is very similar to the hydrolysis/condensation reactions described previously in sol-gel processes.¹⁶ An example of the overall reaction proposed for the thio 'sol-gel' process between $[\text{Ti}(\text{SBu}^t)_4]$ and H₂S is shown in equations (1) and (2).



Further evidence for the partial replacement of -SR ligands by -SH groups in the thio 'sol-gel' step was obtained from the elemental analytical data (C, H and N) for the precipitates, as shown in Table 1. Thus, the carbon content of the precipitates was found to be lower than in the thiolate precursors themselves which is expected if -SR groups are replaced by -SH. The thiolate $[\text{Ti}(\text{SBu}^t)_4]$ was prepared as described in the literature,⁴ however after repeated recrystallisations a small amount of nitrogen was still present in the compound (calc. %C 47.5, %H 8.97, %N 0.0; found %C 47.25, %H 9.01, %N 0.71). This is probably due to impurities from the starting

Table 1 Elemental analytical data (CHN) for the thiolate precursors and the precipitates

Thiolate precursor	Thiolate precursor			Precipitate		
	%C	%H	%N	%C	%H	%N
$[\text{Ti}(\text{SBu}^t)_4]^a$	47.25	9.01	0.71	21.10	3.69	3.67
$[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2^b$	40.06	2.28	2.84	32.24	4.06	4.05
$[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]^b$	38.83	2.10	3.17	17.53	2.28	2.80
$[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]^c$	60.07	5.60	1.04	24.01	4.97	2.68

^aRef. 4; %C 46.7, %H 8.82 reported. ^bAs reported in ref. 18 for $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2$ and $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$. ^cAs reported in ref. 17. for $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$.

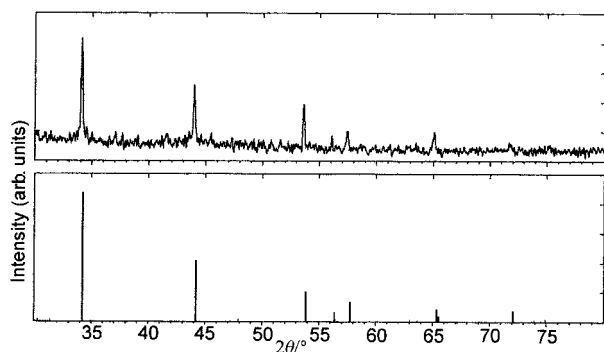
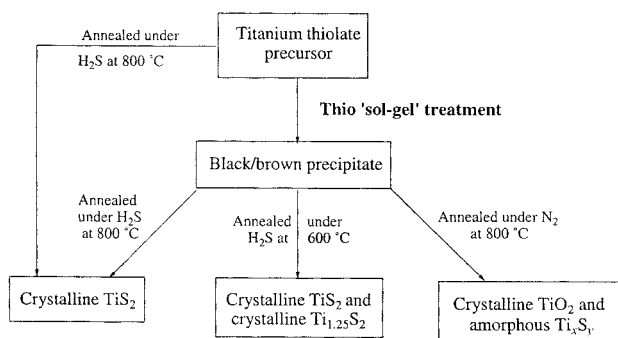


Fig. 1 Top trace: X-ray powder diffraction pattern of TiS_2 prepared by annealing the precipitate (obtained from thio 'sol-gel' reaction of $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ with H_2S) under H_2S at 800°C . Bottom trace: literature stick pattern for TiS_2 .

titanium(IV) amido complex, $\text{Ti}(\text{NET}_2)_4$, and it accounts for the presence of nitrogen in the precipitate obtained. Powder XRD of the precipitates²⁰ revealed they were X-ray amorphous. It was therefore decided to anneal the amorphous precipitates under a variety of conditions, as shown in Scheme 2, in an attempt to convert the precipitates to crystalline TiS_2 .

Initial attempts to convert the amorphous precipitates to crystalline TiS_2 involved the heat treatment of the precipitate in flowing H_2S gas at 800°C . A temperature of 800°C was initially chosen based on related conversions of amorphous precipitates (formed by the thio 'sol-gel' reaction of $[\text{Ti}(\text{OR})_4]$ with H_2S) to crystalline TiS_2 as reported previously.^{13–15} In all cases a black solid formed after annealing at 800°C except when $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_9]$ was used as the initial thiolate precursor, in which case a black solid with a gold surface resulted. Powder XRD of the material²⁰ showed that a single phase of hexagonal TiS_2 had formed (Table 2) with a typical crystallite size from the X-ray broadening of 800 \AA . Fig. 1 shows the powder XRD pattern of TiS_2 prepared *via* this route from $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$. The X-ray powder pattern of the TiS_2 obtained was indexed and gave exact matches to



Scheme 2

Table 2 X-Ray powder diffraction data^a for TiS_2 obtained after annealing thio 'sol-gel' precipitates to 800°C under H_2S

Starting thiolate precursor	Lattice parameters of TiS_2 ^b obtained			
	Thio 'sol-gel' step		No thio 'sol-gel' step	
	<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>
$[\text{Ti}(\text{SBU})_4]$	3.415	5.705		
$[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2$	3.409	5.699		
$[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$	3.417	5.724	3.400	5.692
$[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_9]$	3.409	5.710	3.405	5.706

^aUnit cell dimensions *a*, *c* in \AA ($\pm 0.005 \text{ \AA}$). ^bLiterature values for TiS_2 : *a* = 3.4049; *c* = 5.6912.²¹

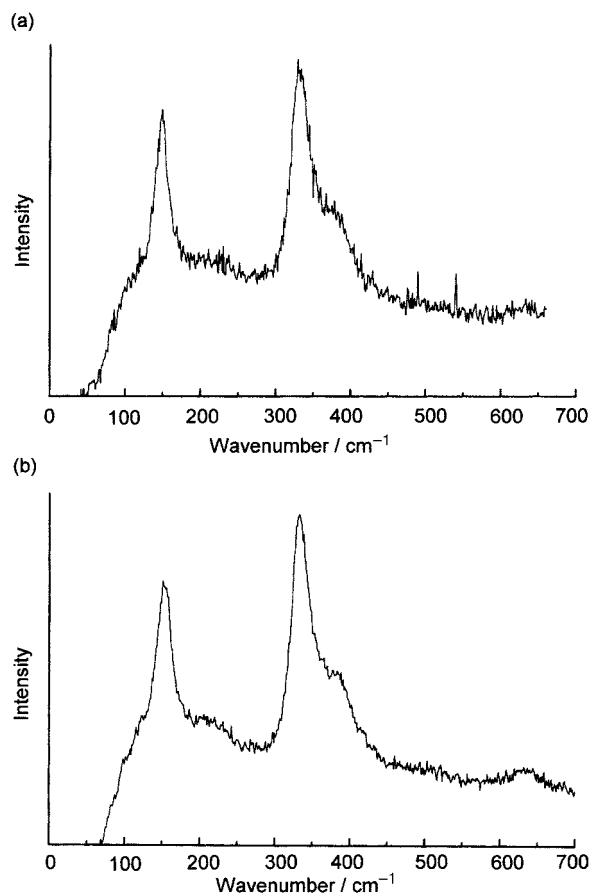


Fig. 2 (a) Raman spectrum for TiS_2 prepared by annealing the precipitate (obtained from the thio 'sol-gel' reaction of $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ with H_2S) under H_2S at 800°C . (b) Raman spectrum of a sample of TiS_2 purchased from Aldrich.

literature measurements (Table 2).²¹ The EDXA data showed good agreement to a 1 : 2 ratio of Ti : S over a number of spots. Fig. 2(a) shows the Raman spectrum of the TiS_2 prepared and this is in good agreement with the Raman spectrum of a sample of TiS_2 purchased from Aldrich [Fig. 2(b)]. Similar results were reported from the annealing at 800°C of the precipitates formed from the thio 'sol-gel' reaction of $[\text{Ti}(\text{OR})_4]$ and H_2S .¹⁴ In these reactions, the formation of single phase TiS_2 was observed, however, at lower temperatures (600°C) a mixture of TiS_2 and rutile and anatase phases of TiO_2 were formed.¹⁴

In order to establish if a temperature of 800°C was necessary to form TiS_2 the precipitate obtained from $[\text{Et}_2\text{NH}_2]_3[\text{Ti}(\text{SC}_6\text{F}_5)_5][\text{SC}_6\text{F}_5]_2$ was annealed at 600°C under a constant flow of H_2S gas. Powder XRD of the resulting black solid²⁰ showed that a mixture of crystalline TiS_2 and $\text{Ti}_{1.25}\text{S}_2$ was formed. However, the EDXA data showed good agreement to a 1 : 2 ratio of Ti : S over a number of spots, suggesting the

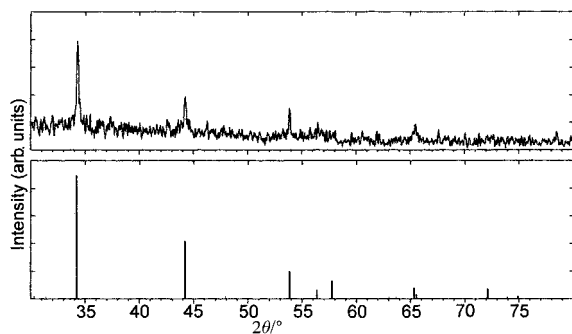


Fig. 3 Top trace: X-ray powder diffraction pattern of TiS_2 prepared by heating $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ under H_2S at 800°C . Bottom trace: literature stick pattern for TiS_2 .

formation of TiS_2 . A temperature greater than 600°C is probably required to form pure crystalline TiS_2 although a mixture of crystalline titanium sulfides can be formed at this temperature without any impurities from TiO_2 . This suggests an advantage of using a titanium thiolate precursor over a titanium alkoxide, since with the latter a mixture of TiS_2 and TiO_2 is formed at 600°C .

With a view to determining if the presence of H_2S is necessary to enable the precipitate to be converted to TiS_2 , it was decided to anneal the precipitate under N_2 . Accordingly, the precipitates from the thio 'sol-gel' reaction were heated under a flow of N_2 at 800°C resulting in the formation of black solids. Powder XRD of the materials²⁰ showed peaks characteristic to anatase but no evidence of crystalline TiS_2 . Furthermore, the EDXA data showed a low sulfur content (Ti:S ratio varied from 1:1 to 7:3) suggesting that either oxidation and/or decomposition had occurred with the formation of some TiO_2 . It is possible that air got into the system during heating, however previous pyrolysis studies on $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$ where the sample was heated under vacuum to temperatures of up to 1000°C showed that only microcrystalline Ti_2S_3 can be made.¹⁷ It seems unlikely at this stage that crystalline TiS_2 can be made without the presence of H_2S gas.

Finally, in order to determine the influence of the initial thio 'sol-gel' step on the nature of the product obtained, it was decided to eliminate this step. Thus, the thiolate precursors $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$ and $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ were heated under a constant flow of H_2S gas at 800°C for 6 hours. A black solid was formed for $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$ and for the thiolate $[\text{Et}_2\text{NH}_2][\text{Ti}_2(\text{SCH}_2\text{Ph})_6]$ a black solid with a gold surface resulted. Powder XRD of the material²⁰ showed that a single phase of hexagonal TiS_2 had formed with a typical crystallite size from the X-ray broadening of 800 \AA . Fig. 3 shows the powder XRD pattern of TiS_2 prepared *via* this route from $[\text{Et}_2\text{NH}_2][\text{Ti}(\text{SC}_6\text{F}_5)_4(\text{NEt}_2)]$. The X-ray powder patterns of the TiS_2 obtained was indexed and again gave exact matches to literature measurements (Table 2).²¹ The EDXA data showed good agreement to a 1:2 ratio of Ti:S over a number of spots. In addition, the Raman spectrum of the TiS_2 prepared was very similar to that obtained from a standard sample of TiS_2 . The formation of crystalline TiS_2 by heating the thiolate precursors under H_2S at 800°C suggests that the thio 'sol-gel' step is not necessary. However, the material produced without the initial thio 'sol-gel' step is much more air sensitive and therefore more difficult to handle. The difference in air sensitivity of the two samples is

attributed to a variation in porosity and surface area within the materials.

In conclusion, a novel thio 'sol-gel' process in which titanium thiolates act as the metal source have been described. In these reactions, a precipitate with a lower carbon content than the starting thiolate precursors is formed, suggesting that some of the thiolate ligands are replaced by $-\text{SH}$ groups. The conversion of these precipitates to TiS_2 is dependent on the conditions of the heat treatment step. Thus, if the precipitates are annealed under H_2S either a mixture of crystalline titanium sulfides (600°C) or crystalline TiS_2 (800°C) is formed. However, annealing the precipitates under N_2 results mainly in the formation of crystalline TiO_2 . The thio 'sol-gel' step does not seem to have a significant influence on the product obtained since the thiolate precursors when heated under H_2S at 800°C result in the formation of crystalline TiS_2 . Nevertheless, the thio 'sol-gel' step allows the formation of less air sensitive products.

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