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The thio-sol–gel synthesis of titanium disulfide and niobium disulfide

Part 1.—Materials chemistry

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Investigations pertaining to the synthesis of titanium disulfide (TiS_2) have so far been focused on solid state reactions, low temperature chemical techniques and vapor phase reactions using titanium tetrachloride ($TiCl_4$) as the starting material. In this paper, we have investigated the potential of titanium tetraalkoxides [$Ti(OR)_4$], which have been widely used for the synthesis of oxides by the sol–gel approach, for the synthesis of TiS_2 *via* the thio-sol–gel process. The mechanism of the reaction of titanium isopropoxide {$Ti(OPr^i)_4$} with H_2S in benzene has been studied using infrared spectroscopy (FTIR), gas chromatography (GC) and chemical analysis. Based on these studies, it has been determined that the precipitate obtained from the reaction forms following a thiolysis–condensation mechanism similar to the hydrolysis–condensation mechanism that operates in the oxide sol–gel process. The precipitate, which is an alkoxysulfide, can be converted to TiS_2 by heat treatments in flowing H_2S. The influence of modifying agents, the role of solvents and the alkoxy group [in $Ti(OR)_4$] on the formation of the alkoxysulfide precipitate have also been presented and discussed. Finally, the applicability of this process for the synthesis of NbS_2 has also been demonstrated.

1 Introduction

Titanium disulfide (TiS_2) has been studied as a useful cathode material for Li intercalation or insertion batteries. It exhibits a strong potential for inserting lithium into the crystal to form Li_xTiS_2, where $0<x<1$, without causing any phase changes. It also has a good electronic conductivity (*ca.* 28 S cm^{-1}) and displays a high reversibility of the intercalation reaction.[1] These properties of the material have made it a viable cathode material for both bulk and thin film rechargeable lithium batteries. The performance of the sulfide as a cathode material depends on the efficacy of the intercalation reaction, which in turn depends on a number of factors such as morphology, crystallite and particle sizes, and defect concentration. All these factors are strongly influenced by the nature of the processes and the processing conditions used to synthesize the material.

There are several methods reported in the literature for synthesizing titanium disulfide in both powder and film form. These methods include: (a) high temperature solid state reactions,[2,3] (b) vapor phase reactions[4–9] and (c) low temperature chemical precipitation techniques.[10,11] The simplest method is the synthesis of the sulfide by melting the individual elements in an evacuated sealed quartz tube at high temperatures. Several vapor phase reactions have also been investigated to synthesize TiS_2 powders and thin films, the most common being the reaction of $TiCl_4$ with H_2S (incidently, this was also the first vapor phase reaction to be investigated for the synthesis of TiS_2 powders[4]). Room temperature chemical precipitation routes mostly using chlorides and various inorganic[10] and organic[11] sulfidizing agents have also been successfully implemented to synthesize fine particles of TiS_2.

All the methods described above result directly in the formation of TiS_2. The low temperature precipitation routes result in a poorly crystalline sulfide which can be crystallized by heating the material at a higher temperature. These precipitates are often contaminated by chloride (Cl^-) ions and by inorganic by-products of the reaction. More importantly, the composition of the material (and therefore its defect structure), its morphology and particle size are all determined at the precipitate stage itself. Therefore there is little flexibility offered by these processes with respect to control of the morphology or stoichiometry of the sulfide. Considering the strong impact of all these factors on the performance of the sulfide as a cathode in rechargeable lithium batteries, it is useful to identify a process that provides this flexibility to control both the microstructure (morphology, particle and crystallite size) and defect concentration of the final sulfide powder.

Metal alkoxides are unique in these sense that they offer the possibility to react with nucleophilic sulfidizing agents to yield precursors which can be converted to form the sulfide with control of defect concentration and microstructure. Metal alkoxides have been extensively investigated for the synthesis of oxide ceramics, glasses and thin films *via* the sol–gel process. However, there has been little work reported on the potential of these compounds for the synthesis of non-oxides.[12–22] In the first part of this two-part series, we report mainly the solution and precursor chemistry pertaining to the synthesis of TiS_2 *via* the thio-sol–gel process. In the second part (see following paper), the morphology, defect concentration and electrochemical characteristics of the thio-sol–gel synthesized TiS_2 powders are presented and discussed.

2 Experimental procedure

The reactions of titanium alkoxides were studied using different sulfidizing agents. At the same time, the influence of modifying the alkoxide, the alkyl group and the solvent system on the sulfidization reaction were also studied. Unless otherwise mentioned, the source and purity of the chemicals and the instruments used for the analyses are: $Ti(OPr^i)_4$ (as received from Johnson Matthey Alfa, 97%), benzene (as received anhydrous benzene from Aldrich, 99.8%), KBr (FT-IR grade from Aldrich, 99+%), CsI (Aldrich, 99.9%), H_2S (Mattson gases, CP grade), benzenesulfonic acid (Aldrich, tech. grade), acetonitrile (anhydrous, as received from Aldrich, 99.8%), ethyl alcohol (absolute, McCormick Distillation Co., Pekin, IL), titanium tetraethoxide (Aldrich, tech. grade), titanium *n*-butoxide (Aldrich, 99%), titanium 2-ethyl hexoxide (Aldrich, 95%), dimethyl disulfide (Aldrich, 99%), hexamethyldisilthiane (Fluka); Gas chromatography (Hewlett Packard model 5830A), mass spectrometry (VG Analytical, model 7070),

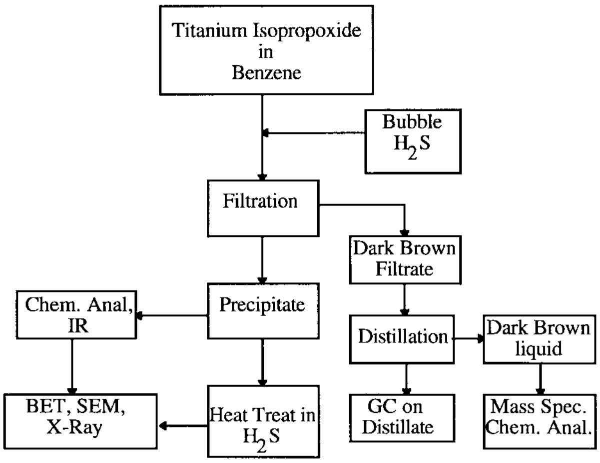


Fig. 1 Schematic flow chart showing the procedure for synthesizing TiS_2 using the reaction of titanium alkoxide with H_2S.

scanning electron microscopy (CamScan series 4). All manipulations and handling of reactants and products were executed under an argon or a nitrogen atmosphere. All reactions were conducted in glassware dried in vacuum at 120 °C after rinsing with hexane.

2.1 Reaction of titanium isopropoxide with H_2S (reaction A)

The flow chart in Fig. 1 describes the experimental procedure. $Ti(OPr^i)_4$ was dissolved in anhydrous benzene, and H_2S was bubbled through it at room temperature. A black precipitate was observed within a minute, but the bubbling was continued for 10 min to ensure completion of the reaction. The reaction vessel was sealed and isolated for 12 h.

The precipitate was then collected and washed thoroughly with anhydrous benzene in a Soxhlet extractor, and dried in vacuum at 40 °C for 3 h after which it was perceived to be pyrophoric and extremely air-sensitive. This precipitate formed the precursor for synthesizing titanium disulfide (TiS_2). Chemical analysis of the precipitate was conducted by Galbraith Laboratories Inc. (Knoxville, TN), and an IR spectrum was collected in the 4000 to 650 cm^{-1} wavenumber range in a KBr pellet using a Fourier transform infrared spectrometer (FTIR spectrometer, Bruecker Instruments) equipped with an MCT detector and in the 500 to 200 cm^{-1} range in a CsI pellet using an FTIR spectrometer (Biorad) equipped with a DTGS detector and CsI optics.

The filtrate obtained was dark brown indicating the presence of molecular species containing Ti—S bonds. The filtrate was azeotropically distilled and gas chromatography (GC) performed on the distillate to quantify the products of the reaction. After ensuring that all the excess benzene was distilled off, chemical analysis was performed on the dark brown liquid. The liquid was also analyzed employing electron impact mass spectroscopy.

2.2 Influence of modification on the reaction of $Ti(OPr^i)_4$ with H_2S

Modification of titanium isopropoxide cannot be accomplished by aqueous acids because of the extreme sensitivity of the alkoxide to water. However, it has been shown that alkoxides react with organic acids to form the metal acylates with the release of alcohol. For example with a carboxylic acid:[23]

$$M(OR)_n + m\ RCOOH \rightarrow M(OR)_{n-m}(OOCR)_m + m\ ROH \qquad (1)$$

In this study, benzenesulfonic acid (BSA, $C_6H_5SO_3H$) was used to modify the alkoxide for the following reasons: (a) BSA is a strong organic acid and (b) it is monofunctional and does not chelate the metal atom (unlike carboxylic acids which chelate the metal atom due to the presence of the highly polar C=O group). In order to confirm the reaction of $Ti(OPr^i)_4$ with BSA, the reactions were conducted in a benzene solvent (in an acid : alkoxide molar ratio, $n = 1:10$, $1:1$ and $2:1$). The isopropanol liberated from the reaction was azeotropically distilled under ultrahigh purity (UHP) nitrogen and quantitatively analyzed using GC.

2.2.1 Modification using the ratio $n = 0.1$ (reaction B). The procedure adopted to study the molecular processes that occur in the reaction of modified alkoxide with H_2S was very similar to that developed for the first reaction. The alkoxide was modified with BSA (n = acid : alkoxide molar ratio = 0.1) in benzene and reacted with H_2S. The precipitate, filtrate and distillate were analyzed as described in section 2.1.

2.2.2 Modification using the ratio $n = 1$ and $n = 2$. Benzenesulfonic acid was added to $Ti(OPr^i)_4$ in benzene in a molar ratio of 1 : 1. When H_2S was passed through the solution for about 10 minutes, there was only a change in the color of the solution from colorless to dark brown, without the appearance of any precipitate. The vessel was left sealed for about 18 h after which the liquid turned black without the formation of any precipitate. $Ti(OPr^i)_4$ was also modified using 2 moles of BSA per mole of alkoxide. When H_2S was bubbled through this solution in benzene, the solution changed from colorless to yellow without the formation of any precipitate. These reactions were not studied any further.

2.3 Influence of solvent on the reaction of $Ti(OPr^i)_4$ with H_2S

Acetonitrile (ACN). Both reaction A (plain alkoxide + H_2S) and reaction B (modified alkoxide + H_2S, using a modification ratio $n = 0.1$) were conducted in anhydrous ACN. In both cases, there was immediate precipitation without any changes in the color of the solution. The precipitates were collected using a Soxhlet extractor, washed with ACN and dried at 40 °C for 3 h. The precipitates were weighed to estimate the yield of the reaction and their Ti and S contents were analyzed to estimate the extent of the sulfidization reaction.

Ethyl alcohol. Neither the plain alkoxide nor the modified alkoxide reacted with H_2S in a solution of absolute ethyl alcohol. A slight color change to light yellow was observed but no precipitate appeared even after allowing the reaction to proceed for several days.

2.4 Influence of alkoxy group on the reaction of alkoxide with H_2S

Three other alkoxides were reacted with H_2S in benzene and in acetonitrile: titanium ethoxide $\{Ti(OC_2H_5)_4\}$, *n*-butoxide $\{Ti(OCH_2CH_2CH_2CH_3)_4\}$ and 2-ethylhexoxide $\{Ti[OCH_2CH(C_2H_5)(CH_2)_3CH_3]_4\}$. The observations are shown in Table 1. The solids collected from the reactions shown in Table 1 were analyzed for their Ti and S contents. The powders were also weighed to estimate the yield of the reactions.

2.5 Reaction of titanium isopropoxide with other sulfidizing agents

2.5.1 $Ti(OPr^i)_4$ + dimethyldisulfide (DMDS; reaction C). $Ti(OPr^i)_4$ was dissolved in anhydrous benzene and excess dimethyl disulfide (DMDS) was added to it. The mixture was refluxed for 24 h at 70 °C, after which a small amount of H_2S gas was passed over the surface of the liquid. This resulted in the formation of a black precipitate. The precipitate was washed with benzene and dried under vacuum at 40 °C for 2 h. The mechanism of the reaction, however, has not been

Table 1 Reaction of titanium alkoxides in benzene and acetonitrile

	Observations	
Alkoxy group	In benzene	In acetonitrile
Ethoxy	Orange soln., no ppt.	Insoluble. Introduction of H_2S for 10 min led to a thick viscous liquid. Some solid collected by heating the liquid under vacuum at *ca.* 60 °C.
n-Butoxy	Dark brown liquid, no ppt.	Insoluble. Introduction of H_2S for *ca.* 5 min led to a black precipitate. The precipitate was washed with acetonitrile and dried at 40 °C for 3 h.
2-Ethylhexoxy	No reaction	No reaction

studied. A similar scheme has been attempted by Guiton *et al.*,[24] where they observed that the reaction of diethylzinc with dibenzyl trisulfide in the presence of H_2S led to an enhancement in the kinetics of precipitation of ZnS.

2.5.2 $Ti(OPr^i)_4$ + hexamethyldisilthiane (HMDST, reaction D). Owing to the extreme moisture sensitivity, coupled with the toxicity and stench of hexamethyldisilthiane (HMDST), a cannula technique was used inside a glove bag for all transfer procedures. HMDST was added to $Ti(OPr^i)_4$ in anhydrous benzene and the vessel was sealed and isolated for 12 h. A change in the color of the mixture from colorless to bright yellow was observed within about 3 min and after a series of color changes, from yellow to dark brown, a black precipitate was finally observed after *ca.* 3 h. The precipitate was collected, washed and dried as described in previous sections. An FTIR spectrum was collected on the precipitate and chemical analysis was conducted to estimate the amounts of Ti, S, C, H and Si in the precipitate.

2.6 Conversion of the precursors to TiS_2

The dried powders obtained from the four reactions (reactions A–D) were then heat treated in flowing H_2S at 600, 700 and 800 °C for 6 h (heated at 15 °C min^{-1} and furnace cooled). At each stage, an X-ray diffractogram was collected using Cu-Kα radiation from $2\theta = 10°$ to 90° (Rigaku θ/θ diffractometer equipped with a diffracted beam graphite monochromator), and the powders were observed under an SEM. Samples for SEM examination were prepared by ultrasonicating the powders in hexane for 5 min and placing a few drops of the suspension on a graphite surface.

2.7 Synthesis of niobium disulfide

Reaction of H_2S with niobium(V) ethoxide. The applicability of the thio-sol–gel process was also extended to the synthesis of NbS_2. Niobium pentaethoxide [$Nb(OC_2H_5)_5$; 10 g] was dissolved in 200 cm^3 acetonitrile. H_2S was passed through the solution for 10 min. A black precipitate was observed to form in 20 s and the vessel was left sealed for 24 h. A Soxhlet extractor was used to filter the suspension and wash the powders using acetonitrile (HPLC grade, used as received from Fisher Chemicals). In this case too, the filtrate was dark brown to black. The black precipitate obtained after filtration was dried under vacuum at 40 °C for 2 h. Absorption IR spectra were collected on the precipitate using the CsI pellet method (using a Mattson Galaxy Series spectrometer equipped with CsI optics) in the wavelength range from 4000 to 200 cm^{-1}. The precipitated powder was then heat treated at 700 and 800 °C for 6 h in flowing H_2S (heated at 15 °C min^{-1} and furnace cooled). X-Ray diffraction patterns were collected on the powders to verify the phases present and the powders were examined in an SEM.

Reaction of H_2S with niobium(V) ethoxide modified with benzenesulfonic acid. Niobium ethoxide was reacted with BSA in the molar ratio of 10 : 1, alkoxide to acid and dissolved in acetonitrile. H_2S gas was bubbled into the solution. The reaction proceeded in the same way as described above. A black precipitate was formed, which was also dried at 40 °C for 2 h under vacuum. IR analysis and further heat treatments of the precipitate were conducted in the same manner as described above.

3 Results and Discussion

In this section, the mechanisms of the reaction of titanium isopropoxide with various sulfidizing agents are presented and discussed along with the influence of solvents and the alkoxy group. This is followed by a study of the conversion of the precipitates obtained from these reactions to crystalline TiS_2. In order to facilitate the discussion, we have used the following abbreviations for the various reactions. Reaction A: the reaction of titanium isopropoxide with H_2S conducted in benzene. The same reaction conducted in acetonitrile will be termed 'reaction A in acetonitrile'. Reaction B: the reaction of titanium isopropoxide modified with BSA using a modification ratio $n = 0.1$, conducted in benzene. Reaction C: the reaction of titanium isopropoxide with dimethyldisulfide (DMDS) catalyzed by H_2S using benzene as a solvent. Reaction D: the reaction of titanium isopropoxide with hexamethyldisilthiane (HMDST) conducted in benzene.

3.1 Reaction of titanium isopropoxide with H_2S (Reaction A)

The IR absorption spectrum collected on the precipitate obtained from the reaction is displayed in Fig. 2, showing the 1800 to 900 cm^{-1} and 500 to 200 cm^{-1} (inset) spectral ranges. The doublet at 1377 and 1360 cm^{-1} is characteristic of the *gem*-dimethyl structure of the isopropoxy group.[25,26] Bands at 1160, 1127 and 1013 cm^{-1} are also characteristic of the isopropoxy groups bonded to Ti.[26] The inset shows the typical Ti—S stretching absorption[10] at 300 cm^{-1} (hence indicating the formation of Ti—S bonds due to the reaction of H_2S with the alkoxide in solution), and the Ti—O stretching absorption at 450 cm^{-1} (owing to the unreplaced isopropoxy groups[25,26]).

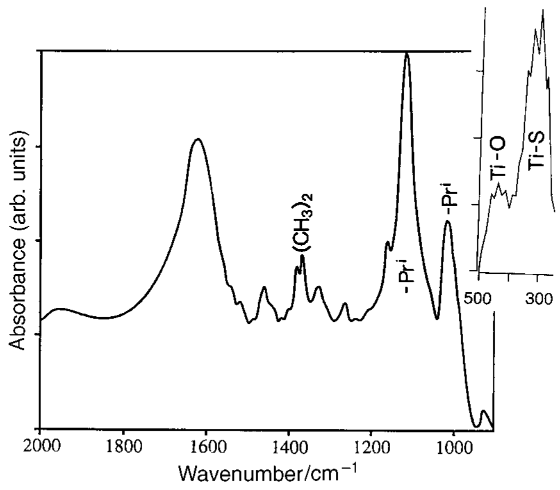


Fig. 2 The IR spectrum collected on the as-precipitated alkoxy-sulfide powder (prepared using reaction A) in the wavenumber range 4000–650 cm^{-1} showing the presence of unreacted isopropoxy groups (1377, 1360, 1160, 1122, 1013 cm^{-1}) bonded to titanium. The inset shows Ti–O and Ti–S absorptions in the far IR range. Note: the absorbance axis has arbitrary units.

Table 2 Chemical analyses and quantitative GC (reaction A)

(a) Chemical analyses of liquid and solid products

	Ti	S	C	H	O (difference)	Weight/g
Solid (wt%)[a]	33.6	32.3	17.3	3.5	13.3	0.754
Solid (mol%)	9.4	13.5	19.3	46.8	11	
Liquid (wt%)[b]	7.3	0.3	76.8	8.1	7.5	30.088
Liquid (mol%)	1	0.06	42.3	53.5	3.1	

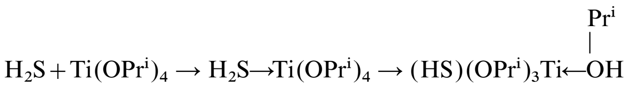
(b) Correlation of isopropanol replacement from chemical analyses and GC

Moles of titanium isopropoxide used in the reaction	0.0504
Moles of isopropanol detected in the distillate	0.025
Moles of isopropanol that should be liberated, calculated from chemical analyses and assuming reaction (4) for all thiol groups	0.021

[a] The solid precipitate was analyzed after drying at 40 °C for 2 h in vacuum. [b] The liquid was analyzed after removing benzene by distillation.

Based on the chemical analysis of the precipitate (shown in Table 2) and the IR results, it can be concluded that the solid is an alkoxysulfide, containing (a) unreacted isopropoxy groups and (b) sulfur bonded to Ti.

Isopropanol was also detected in the distillate implying the replacement of isopropoxy groups (OPr^i) by thiol groups (SH) from H_2S. This attack of the alkoxy groups would form the basis of a thiolysis reaction very similar to the hydrolysis reactions in the sol–gel process, as illustrated by Livage:[27]



$$H_2S+Ti(OPr^i)_4 \rightarrow H_2S{\rightarrow}Ti(OPr^i)_4 \rightarrow (HS)(OPr^i)_3Ti{\leftarrow}\overset{\overset{\displaystyle Pr^i}{|}}{O}H$$

$$\rightarrow Ti(OPr^i)_3SH+Pr^iOH \qquad (2)$$

The overall reaction can therefore be written as

$$Ti(OPr^i)_4+nH_2S \rightarrow Ti(OPr^i)_{4-n}(SH)_n+nPr^iOH\ (n<4) \qquad (3)$$

After thiolysis, the precipitates could have formed due to condensation–polymerization of the alkoxythiols by the liberation of H_2S as explained in the following paragraphs:

$$2p\ \{Ti(OPr^i)_{4-n}(SH)_n\} \rightarrow \{(Pr^iO)_{4-n}(SH)_{n-1}Ti\text{-}S\text{-}Ti(SH)_{n-1}(OPr^i)_{4-n}\}_p+pH_2S\,(n<4) \qquad (4)$$

The condensation of alkoxy groups is less likely due to the highly polar character of the Ti—O bonds as well as steric hindrance caused by the bulky isopropoxy groups.

As shown in Table 2, 0.025 moles of alcohol per 0.0504 moles of starting Ti isopropoxide, was detected by quantitative GC. It should be noted that the alcohol released is a result of the alkoxythiol ($OPr^i{\leftrightarrow}SH$) replacement reaction responsible for the formation of both the liquid and the solid products. In order to confirm the formation of the precipitate by the above mentioned condensation mechanism [reaction (4)], the isopropanol liberated was calculated from the chemical analysis of the liquid and solid products. Assuming that the precipitates are formed as a result of condensation of all the thiol groups leaving sulfur formally bonded to two titanium atoms, calculations indicate an expected release of 0.021 moles of isopropanol, which is in good agreement with the isopropanol content estimated by quantitative GC. This, therefore, validates the assumed condensation mechanism. Two facts, therefore, become clear from the above analysis: (a) infrared spectroscopy and GC have indicated that the thiolysis reaction as shown in reaction (3) causes partial replacement of OPr^i with SH, (b) GC in conjunction with chemical analyses confirm condensation of thiols to be the dominant mechanism.

Chemical analysis of the liquid product (Table 2) showed a S/Ti molar ratio of about 0.06. In addition, the mass fragmentation pattern of the liquid was identical to that of titanium isopropoxide, implying that the dark liquid was in fact Ti isopropoxide, which had not undergone any significant reaction with H_2S. Some of the alkoxide molecules remained unreacted, possibly due to (a) association in inert solvents like benzene (titanium isopropoxide is known to have an average molecular complexity of 1.3 in benzene[28]), or (b) due to the formation of partially reacted soluble oligomers which do not undergo any further reaction in benzene because of steric hindrance to nucleophilic attack by H_2S. Experiments conducted in acetonitrile (a coordinating solvent which is known to be a better medium for the dissociation of H_2S), have shown more than a five-fold increment in product yield, providing support for this hypothesis. Increase in the product yield when the reaction was conducted in ACN led us to explore the effects of solvent and alkoxy groups on the yield of the reaction. These results are presented in the following sections.

3.2 Influence of modification

Titanium isopropoxide dissolved in benzene was modified using BSA in the modification ratios (n = molar ratio of acid to alkoxide) of 0.1, 1 and 2. The isopropanol liberated from the reaction was azeotropically distilled and quantitatively analyzed using gas chromatography. Based on the number of moles of isopropanol liberated, we could confirm that the following modification reaction went to completion:

$$Ti(OC_3H_7)_4+n\ C_6H_5SO_3H{\rightarrow}Ti(OC_3H_7)_{4-n}(C_6H_5SO_3)_n +nC_3H_7OH\ (n=0.1,\ 1,\ 2) \qquad (5)$$

The alkoxides, modified to different extents, were reacted with H_2S using anhydrous benzene as a solvent.

3.2.1 Modification using the ratio $n=0.1$ (reaction B) The infrared spectrum of the precipitate obtained from the reaction of the alkoxide (partially modified by benzenesulfonic acid in the molar ratio of 10 to 1, alkoxide to acid) with H_2S is shown in Fig. 3. The most important feature of the spectrum is the existence of absorptions at 1000, 1020 and 1040 cm^{-1} all of which correspond to the sulfonyl vibrations of the acid.[29,30] In addition to this, other vibrations due to the alkoxy groups

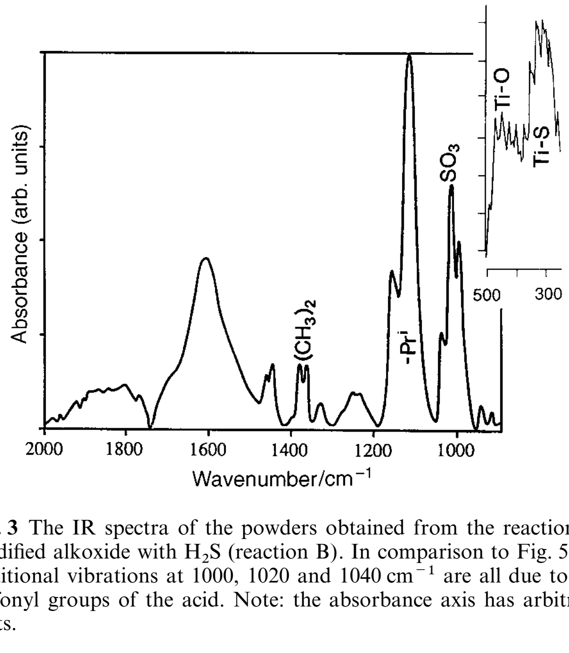


Fig. 3 The IR spectra of the powders obtained from the reaction of modified alkoxide with H_2S (reaction B). In comparison to Fig. 5 the additional vibrations at 1000, 1020 and 1040 cm^{-1} are all due to the sulfonyl groups of the acid. Note: the absorbance axis has arbitrary units.

Table 3 Chemical analyses and quantitative GC (reaction B)

(a) Chemical analysis of liquid and solid products

	Ti	S	C	H	O (difference)	Wt./g
Solid (wt%)[a]	32.3	30.3	20.8	3.5	13.1	1.234
Solid (mol%)	8.8	12.4	22.7	45.3	10.8	
Liquid (wt%)	16.4	1.8	48.5	8.4	24.9	12.3[b]
Liquid (mol%)	2.4	0.4	28.0	58.4	10.8	

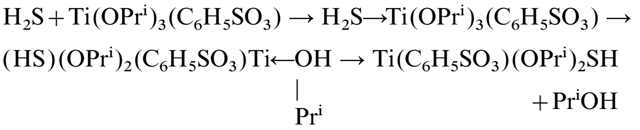
(b) Correlation of replacement of isopropanol from chemical analysis and GC

Moles of titanium isopropoxide used in the reaction	0.0504
Moles of isopropanol detected in the distillate ignoring the isopropanol liberated from the modification reaction	0.016
Moles of isopropanol that should be liberated, calculated from chemical analysis assuming complete thiol based condensation mechanism	0.027

[a] The solid precipitate was analyzed after drying at 40 °C for 2 h in vacuum. [b] Calculated by conserving titanium.

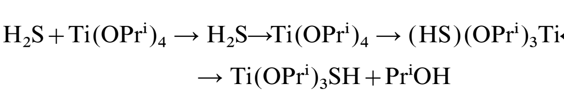
bonded to Ti can be observed (C—O vibrations at 1120 and 1160 cm^{-1}) indicating also the existence of unreacted alkoxy groups in the solid precipitate from the sulfidization reaction. The replacement of some alkoxy groups by SH is of course again confirmed by the presence of the Ti—S vibration at 300 cm^{-1} (see inset in Fig. 3).[10] This replacement has been verified in a manner similar to reaction A, namely by the identification of isopropanol as a by-product of the reaction using a combination of quantitative GC and chemical analysis (see Table 3).

The observations discussed above imply that: (a) the acid reacts to completion with the alkoxide to modify one tenth of the titanium alkoxide molecules as shown in reaction (5) for $n=0.1$ and (b) the sulfonyl group is not replaced by H_2S during the sulfidization reaction, but the molecules of alkoxide that are modified do participate in the thiolysis reactions (no sulfonyl group vibrations could be detected in the IR spectrum of the liquid obtained from the reaction) as do those that are not modified:



$$H_2S + Ti(OPr^i)_3(C_6H_5SO_3) \rightarrow H_2S{\rightarrow}Ti(OPr^i)_3(C_6H_5SO_3) \rightarrow (HS)(OPr^i)_2(C_6H_5SO_3)Ti{\leftarrow}\underset{\substack{|\\ Pr^i}}{O}H \rightarrow Ti(C_6H_5SO_3)(OPr^i)_2SH + Pr^iOH \quad (6)$$

and



$$H_2S + Ti(OPr^i)_4 \rightarrow H_2S{\rightarrow}Ti(OPr^i)_4 \rightarrow (HS)(OPr^i)_3Ti{\leftarrow}\overset{\substack{Pr^i\\ |}}{O}H \rightarrow Ti(OPr^i)_3SH + Pr^iOH \quad (7)$$

After thiolysis, the precipitates form due to the condensation-polymerization of the alkoxythiols by the liberation of H_2S in the same way as shown in reaction (4).

The reaction mechanism can be elucidated further by (a) performing quantitative GC analysis of the benzene–isopropanol azeotrope obtained upon distillation of the filtrate from the reaction and (b) a correlation of this analysis to the results of chemical analysis in a manner similar to that described in the previous section. These results are displayed in Table 3.

The isopropanol observed in the distillate is lower than that calculated from chemical analysis (assuming complete condensation, *i.e.* the condensation of all the Ti—SH groups to form Ti—S—Ti bonds). This implies that part of the sulfur (approximately one third of the number of moles of S) in the solid and the liquid are still not condensed completely leading to the presence of some Ti—SH linkages in the solid, the condensation of which could be sterically hindered due to the presence of the bulky benzenesulfonyl groups.

3.2.2 Modification using the ratio $n=1$ and $n=2$. When H_2S gas was bubbled into a solution of $Ti(OPr^i)_4$ in benzene modified using a modification ratio of $n=1$, a series of color changes was observed, from colorless to yellow to dark brown, without the formation of any precipitate. The change in color indicated the possibility of some thiolysis reaction occurring in solution leading to the formation of some Ti—SH linkages without any condensation. Similarly, the alkoxide solution modified using the ratio $n=2$ changed from colorless to yellow when reacted with H_2S, again without the formation of any precipitate. This occurs mainly due to steric hindrance offered by the bulky acid groups. In the case of H_2S, even though thiolysis may occur, condensation does not occur because of steric hindrance. These observations are similar to the oxide sol–gel process, wherein the hydrolysis reaction of water with a modified alkoxide is considerably slower than that with an unmodified alkoxide.

3.3 Influence of solvent

To evaluate the effect of solvent, reactions A and B were conducted in a non-polar solvent (anhydrous benzene, described above), a polar protic solvent (absolute ethyl alcohol) and a polar aprotic solvent (anhydrous acetonitrile). The yield of each of the reactions was measured along with the S/Ti molar ratios in the precipitates obtained from the reactions (see Table 4).

It is well known that the HS^- ion is a stronger nucleophile than H_2S. A simple calculation of partial charges on the electronegative species shows that S in H_2S has a partial charge $\delta_S=-0.13$, while in HS^-, $\delta_S=-0.6$. Therefore, a larger concentration of HS^- ions in solution should strongly affect the thiolysis reaction. The dissociation of H_2S to H^+ and HS^- is higher in solvents with a higher relative permittivity. In benzene, molecular H_2S acts as the nucleophile in its reaction with the alkoxide.

It is likely that during thiolysis in benzene, intermediate oligomers form, which are resistant to nucleophilic attack because of steric hindrance hence lowering the overall yield. Electron impact mass spectrometry of the liquid product from the first reaction indeed showed that the mass fragmentation pattern of the liquid fraction from the reaction was similar to that of the plain alkoxide. In acetonitrile, the dissociation of H_2S causes the formation of the stronger nucleophile, HS^-, which can react even with the intermediate species leading to condensation. An interesting point to note is that although ethyl alcohol has a relatively large relative permittivity, comparable to that of acetonitrile, (implying the formation of more HS^- species), the reaction of titanium isopropoxide does not proceed to any significant extent in this solvent. This is because in protic solvents, the anions are solvated by hydrogen bonding from the solvent.[31] Therefore in alcohols, the HS^- ions are solvated by alcohol molecules, which prevent them

Table 4 Molar yield of titanium from reactions A and B in benzene, ethyl alcohol and acetonitrile

Solvent	Relative permittivity	Plain isopropoxide (reaction A)		Modified isopropoxide[a] (reaction B)	
		Yield (%)	S/Ti[b]	Yield (%)	S/Ti[b]
Benzene	2.3	*ca.* 15	1.4	*ca.* 15	1.3
Ethyl alcohol	32.7	—	—	—	—
Acetonitrile	37.5	*ca.* 90	1.3	*ca.* 90	1.5

[a] Modified in a ratio of 10:1, isopropoxide to benzenesulfonic acid. [b] Molar ratio of sulfur to titanium in the precipitated powder.

from attacking the Ti center of the alkoxide (again by steric hindrance). On the other hand, in aprotic solvents like acetonitrile, the cation (H^+) is strongly solvated by solvent molecules because the exposed N atom in acetonitrile carries a significant negative partial charge.[31] The positive end of the dipole is buried in the alkyl group which makes it ineffective in solvating the negative ions (HS^-). This leaves the anions free to participate in the reaction. Therefore, the best solvent system for the thio-sol–gel process involving H_2S as a sulfidizing agent is an aprotic polar solvent.

3.4 Influence of alkoxy group

A total of four different alkoxides of titanium were reacted with H_2S in benzene and in acetonitrile: ethoxide, isopropoxide, *n*-butoxide and 2-ethylhexoxide. The yields of the reactions in benzene and in acetonitrile are shown in Table 5, along with their molecular complexities. The molecular complexity of titanium ethoxide is high because of the small size of the ethoxy group. The larger alkoxy groups show a lower molecular complexity, because complexity itself is reduced by steric hindrance. If we consider the reactions conducted in benzene, the isopropoxide is the only alkoxide of titanium which shows any reaction with H_2S. The ethoxide shows no reaction because of steric hindrance caused by a higher molecular complexity and the larger alkoxides (*n*-butoxide and ethylhexoxide) show no reaction because of hindrance from the bulky alkyl groups, although the larger alkoxides tend to exist as monomers in benzene. In the case of titanium, the isopropoxy group offers the best combination of size, alkyl group and molecular complexity. Hence, the sulfidization reaction is seen to occur to considerable extents using Ti isopropoxide in both polar aprotic and in non-polar solvents.

The ethoxide, *n*-butoxide and ethylhexoxide do not dissolve in acetonitrile. However, when H_2S is bubbled through the suspension, the ethoxide and the *n*-butoxide do react. The ethoxide forms a thick viscous liquid precursor, which forms a glassy solid when dried under vacuum at 60 °C. The solid shows a S to Ti molar ratio of 1.5, which implies a significant extent of the reaction with H_2S (similar to reaction A in benzene or ACN using titanium isopropoxide). It was also observed that the liquid precursor could be easily coated on glass (by dip-coating or spin-coating) to form films which appeared to be quite stable in air. These preliminary observations indicate a potential application of this process for the formation of TiS_2 thin films. The reaction of H_2S with titanium *n*-butoxide also proceeds to a significant extent, the precipitates showing a molar ratio of S to Ti of 1.5 (comparable to reaction A using titanium isopropoxide). The yield from this reaction is also high, although not as high as what is observed in the case of the reaction of H_2S with titanium isopropoxide in the same solvent. Titanium 2-ethylhexoxide does not react with H_2S either in benzene or in acetonitrile because of steric hindrance from the bulky ethylhexoxy group.

In summary, steric hindrance plays a significant role in the reaction of H_2S with alkoxides. Alkoxides with the smallest alkoxy group on the metal center and having the least molecular complexity exhibit the lowest steric hindrance to nucleophilic attack. Such an alkoxide would be most likely to react with H_2S and undergo thiolysis and condensation reactions to form solid precursors useful for the synthesis of sulfides. Similarly, the most appropriate solvent system is a polar aprotic solvent having a large relative permittivity (for example, acetonitrile) which is an effective medium for the dissociation of H_2S to form HS^- species, which are stronger nucleophiles in comparison to H_2S.

Table 5 Reactions of various titanium alkoxides with H_2S in benzene and in acetonitrile

Alkoxide	Molecular complexity[a]	Reaction in benzene Yield (%)	Reaction in benzene S/Ti[b]	Reaction in acetonitrile Yield (%)	Reaction in acetonitrile S/Ti[b]
Ethoxide	2.5	—	—	—[c]	1.5[c]
Isopropoxide	1.3	15	1.4	90	1.3
n-Butoxide	1.4	—	—	80	1.5
2-Ethylhexoxide	1	—	—	—	—

[a] References 28,32. [b] Molar ratio of sulfur to titanium in the solid. [c] A thick viscous liquid was obtained from the reaction. A solid was obtained by heating the liquid under vacuum at 60 °C.

Table 6 Chemical analysis of precursors obtained from reactions C and D

Reaction	Ti	S	C	H	Si	O (difference)
Reaction C (DMDS), wt.%	34.9	28	15.5	3.3	—	18.3
Reaction D (HMDST), wt.%	32	22.5	20	3.3	4.3	17.9

3.5 Reactions of titanium isopropoxide with DMDS and HMDST

The precipitates that resulted from reactions C and D were very air sensitive and extra precautions were taken while handling these powders. Table 6 shows the results of chemical analysis performed on these precursors. It can be observed that the sulfur contents in these precipitates are considerably lower, indicating a lower extent of replacement of the alkoxy groups. In addition, the reaction of the alkoxide with HMDST results in a powder contaminated with Si.

The as-precipitated powders were amorphous, while the IR spectra of the powders showed the same characteristic vibrations corresponding to the presence of isopropoxy groups (in the region of 1800 to 900 cm^{-1}) as seen in the powders prepared using the first two reactions. Ti—O and Ti—S vibrations were also seen at 450 and 300 cm^{-1} respectively. In addition to these absorptions, the powder prepared using HMDST as the sulfidizing agent also showed $\nu_{Si—O}$ and $\delta_{Si(CH_3)_3}$ vibrations at 933 and 757 cm^{-1} respectively.[33]

In reaction C (using DMDS as a sulfidizing agent) there is a possibility of heterolytic cleavage of the S—S bond due to the presence of H_2S, causing the formation of RS^- species which attack the alkoxide.[34] In reaction D the following sequence could operate:

$$\equiv TiOPr^i + R_3Si\text{-}S\text{-}SiR_3 \rightarrow \equiv Ti\text{-}S\text{-}SiR_3 + R_3Si\text{-}OPr^i \quad (8)$$

$$\equiv Ti\text{-}S\text{-}SiR_3 + \equiv Ti\text{-}OPr^i \rightarrow \equiv Ti\text{-}S\text{-}Ti\equiv + R_3Si\text{-}OPr^i \quad (9)$$

(R = methyl group)

At present, the proposed reactions paths are hypothetical and have been proposed based on the properties of the sulfidizing agents and the IR results of the solid precipitates obtained from the reactions. More detailed studies to elucidate the exact reaction mechanisms were not conducted owing to the benefits exhibited by the use of H_2S in reactions A and B.

3.6 Conversion of precursors to TiS_2

Reaction A. The precipitates obtained from reactions A–D were amorphous to X-rays. The X-ray traces obtained on the precipitate obtained from reaction A after conducting different heat treatments are shown in Fig. 4 indicating the formation of crystalline TiS_2 with increasing temperature. At 600 °C, crystalline TiS_2 was observed along with the presence of rutile and anatase phases of TiO_2. The formation of TiO_2 could be explained by the favored high temperature condensation reaction of the unreacted isopropoxy groups:

$$Ti\text{-}OPr^i + Pr^iO\text{-}Ti \rightarrow Ti\text{-}O\text{-}Ti + \text{hydrocarbons} \quad (10)$$

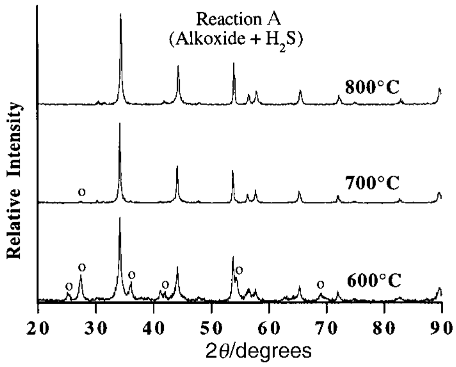


Fig. 4 The X-ray diffractograms of the powders prepared from reaction A, heat treated at 600, 700 and 800 °C for 6 h respectively. The TiS_2 peaks appear at 600 °C along with the rutile and anatase peaks of TiO_2 marked by 'O'. The oxide peak (rutile) is of low intensity at 700 °C and is eliminated at 800 °C.

This process could have occurred at the drying stage as well as during the initial stages of heat treatment. At 700 °C after 6 h in H_2S, only a small amount of oxide is present as evidenced by the relatively low intensity peak visible at $2\theta = 27.5$, implying the reduction of the Ti—O bonds by H_2S in the vicinity of this temperature. We have observed that continued heat treatment at 700 °C for about 10 h can eliminate the oxide phase. At 800 °C, the oxide is completely eliminated, yielding single phase TiS_2. Based on these results, a mechanism for the formation of the sulfide could be postulated as follows. (1) The sulfur containing thiol groups attached to titanium in the amorphous precursor transform in the presence of H_2S to form crystalline TiS_2 at 600 °C, while the unreacted alkoxy groups attached to titanium undergo condensation reactions to form the oxide. (2) The oxide then reacts with H_2S at 700 °C to form the sulfide. (3) It is also possible that some of the sulfur remains bonded to Ti as an oxysulfide. The presence of such oxysulfides of titanium has been reported.[35] Thus, although a portion of the unreacted alkoxide transforms to the sulfide *via* the gas–solid reaction, the formation of single phase TiS_2 at 800 °C in 6 h is an indication of the enhanced kinetics of the sulfidization reaction due to the incorporation of sulfur in the initial stages leading to the formation of the alkoxysulfide precursor. The formation of titania led us to conduct some control experiments employing fine particles of TiO_2 obtained by hydrolyzing titanium isopropoxide in a solution of acetonitrile *via* a sol–gel reaction. The powders were heat treated in H_2S employing the same conditions (800 °C for 6 h) and the results showed TiO_2 to be the major phase. Similar observations have been reported on the formation of cubic La_2S_3[12–15] from the sulfidization of alkoxides. The partially sulfidized lanthanum oxysulfide precursors transform to the crystalline sulfide (La_2S_3) at reduced temperatures and in much shorter reaction times than those reported for the conventional routes involving high temperature sulfidization of sol–gel derived oxide gels in H_2S. The alkoxide approach therefore offers a novel route to the synthesis of sulfide ceramics of reactive metals.

The evolution of morphology of the powders appears to follow an interesting path as displayed in Fig. 5(a)–(d). The as-precipitated powder is spherical and monodispersed with a particle size of about 0.5 μm. The monodispersed particle size distribution points to the fact that the rate of thiolysis is much slower than the rate of condensation.[36] This helps maintain the concentration of the condensing species [shown in reaction (3)] below the critical concentration required for homogenous nucleation. Therefore any new species formed merely condense on the particles already formed during the initial burst of nucleation, hence causing growth. In addition to its molecular structure, the high surface area of the precursor of about $15\ m^2\ g^{-1}$ makes it more sensitive to handling in air, hence several precautions were taken to minimize its exposure to air.

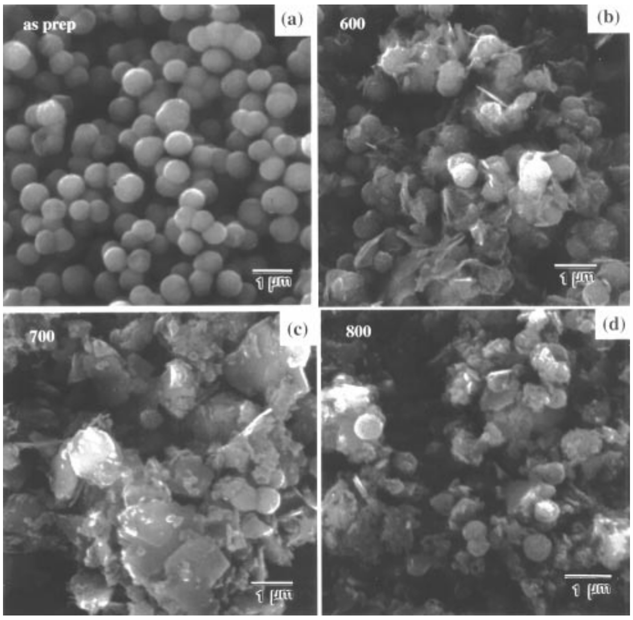


Fig. 5 SEM micrographs of the powders; (a) as-prepared powders from reaction A, and heat treated to (b) 600 °C, (c) 700 °C and (d) 800 °C for 6 h each in flowing H_2S. The micrographs (b)–(d) clearly indicate changes in morphology occurring with the crystallization of TiS_2.

At 600 °C, as shown in Fig. 5(b), small platelets of TiS_2 are seen to form, which are separated from the spherical particles. At 700 and 800 °C however, there are very few spherical particles and some sintering has occurred between the platelets as indicated in the micrographs in Fig. 5(c), (d). The size of the platelets is not uniform and they range in width from 0.5 to 1 μm. Surface area measurements of the powder heat treated at 700 °C have indicated a more than threefold increase to a value of about $52\ m^2\ g^{-1}$.

Reaction B. Conversion of the precipitates obtained from reaction B to TiS_2 was again accomplished by heat treatment in flowing H_2S. The X-ray diffraction patterns of the powders heat treated to various temperatures are shown in Fig. 6. At 600 °C the peaks are broad (in comparison to the corresponding pattern shown in Fig. 4 for the products of reaction A) indicating the presence of fine crystallites. Peaks characteristic of rutile and anatase also appear at this temperature, however heat treatments at higher temperatures of 700 and 800 °C yield single phase hexagonal TiS_2.

The SEM micrographs of the precipitates and heat treated

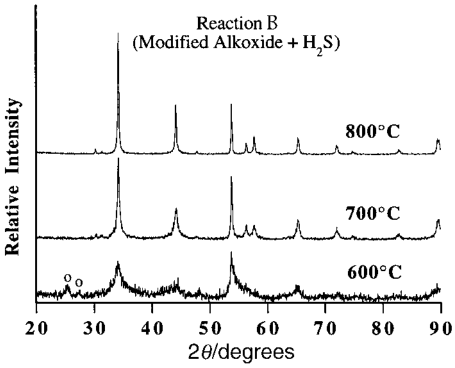


Fig. 6 Powders derived from reaction B heat treated at 600, 700 and 800 °C for 6 h each in flowing H_2S. Peaks marked 'O' are due to TiO_2 (anatase and rutile).

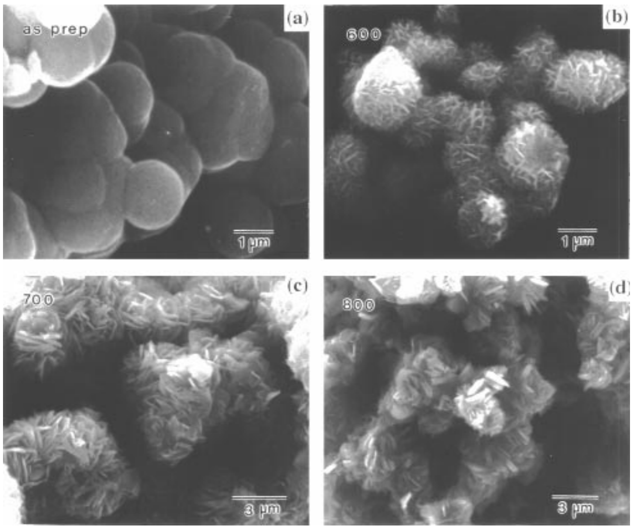


Fig. 7 Morphology of the powders obtained from reaction B (modified alkoxide + H_2S), (a) precipitated powder and the powder heat treated at (b) 600 °C, (c) 700 °C and (d) 800 °C for 6 h each in flowing H_2S.

powders are shown in Fig. 7(a)–(d). The as-precipitated powder consists of agglomerated spherical particles about 2 μm in diameter which are about four times as large as the particles obtained from reaction A. On heat treatment at 600 °C, it can be seen that the TiS_2 crystallites begin to form from individual spherical particles with their prismatic planes directed radially outwards. In this transformation, the spherical shape of the original particles, however, is retained. At 700 °C, the platelets grow further along both basal and prismatic planes while maintaining the overall shape of the agglomerates. At 800 °C, the platelets seem to have grown in both the prismatic and basal plane directions. The morphologies that have formed in this case are distinctly different from those observed in reaction A due to the pseudomorphous transformation of the spherical precipitates to form TiS_2. There is therefore a strong influence of modification of the alkoxide on the evolved morphology of the TiS_2 platelets.

Reactions C and D. X-Ray diffractograms of the precipitates subjected to heat treatments in flowing H_2S are shown in Fig. 8(a), (b). In the case of reaction C (Ti isopropoxide + DMDS + H_2S), the conversion of the alkoxysulfide precipitate to TiS_2 is close to completion upon heat treatment at 600 °C for 6 h (note the low relative intensity of the peak characteristic of titania). The broad TiS_2 peaks grow and sharpen at higher temperatures while the oxide peaks are completely eliminated. On the other hand, the powder obtained from reaction D (Ti isopropoxide and HMDST) shows sharp TiS_2 peaks at 600 °C superimposed on an amorphous background in addition to the oxide (rutile and anatase) peaks of TiO_2 [see Fig. 8(b)]. At 700 and 800 °C, however, single phase TiS_2 is formed.

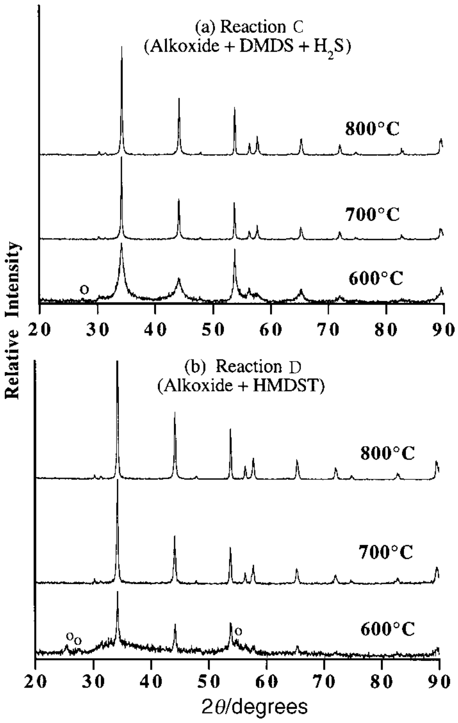


Fig. 8 (a) X-Ray diffractograms of the powders obtained from reaction C (alkoxide + H_2S + DMDS) heat treated at 600, 700 and 800 °C for 6 h each in flowing H_2S. TiS_2 is formed at 600 °C with relatively small amounts of oxide (peak marked 'O'), (b) X-ray diffractograms of the powders obtained from reaction D (alkoxide + HMDST) heat treated in flowing H_2S under the same conditions.

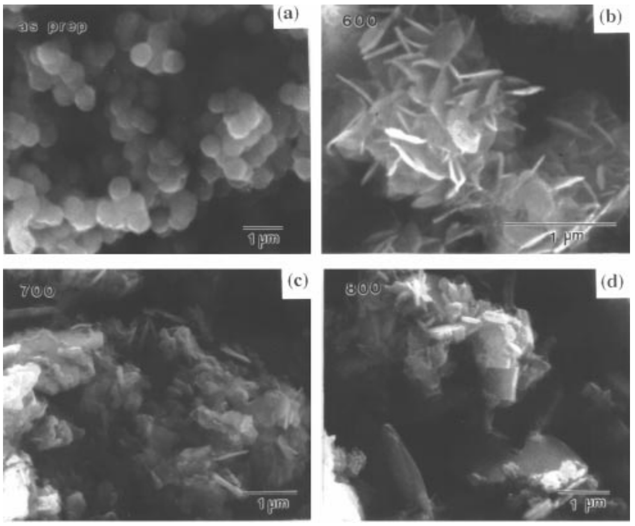


Fig. 9 SEM micrographs of the powders from reaction C; (a) as precipitated, showing monodispersed spherical particles, (b) heat treated at 600 °C, showing the formation of TiS_2 platelets, (c) heat treated at 700 °C and (d) at 800 °C. All heat treatments done for 6 h.

The SEM micrographs of the precipitated precursor and the heat treated powders (obtained from reaction C) are displayed in Fig. 9(a)–(d). The precursor powder shows spherical monodispersed particles of about 0.5 μm in diameter, similar to the powders obtained from reaction A [compare with Fig. 5(a)]. At 600 °C, however, there are no spherical particles remaining, since most of them have transformed (probably along a path similar to that observed in the case of reaction B) to form agglomerates of fine platelets about 0.3 to 0.5 μm along the basal plane. At higher temperatures (700 and 800 °C) there is random growth of the platelets which have basal plane dimensions ranging from a fraction of a micrometer to several micrometers. The as-precipitated precursor powders from reaction D [shown in Fig. 10(a)], however, are quite different; the particles are spherical, but are also polydispersed. They range in size from 0.5 to about 2 μm. At 600 °C, TiS_2 platelets measuring 1 to 2 μm along the basal plane can be seen along with spherical particles which exhibit rough surface features. At 700 °C, however, the morphology is similar to Fig. 7(c), where platelets (about 0.5 to 1 μm) have grown from the spherical precursor particles. On further heat treatment at 800 °C the morphology of the powders show a controlled growth of the platelets in both the basal and prismatic plane directions similar to the characteristic morphology exhibited by the powders obtained from reaction B using BSA [see Fig. 7(d)].

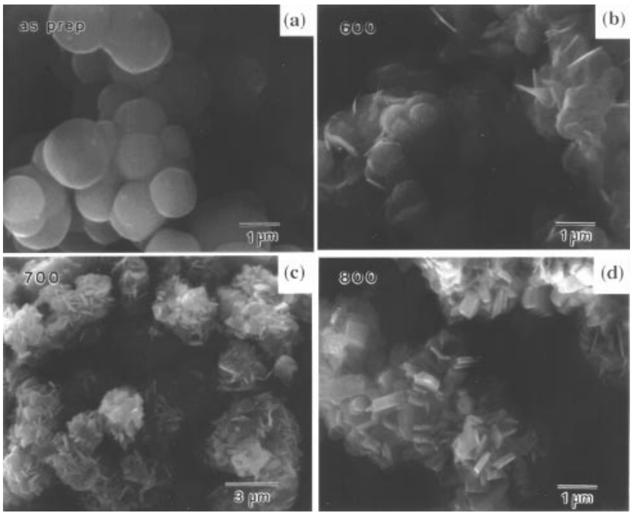


Fig. 10 SEM micrographs of the powders obtained from reaction D; (a) as-precipitated and heat treated for 6 h at (b) 600 °C, (c) 700 °C and (d) 800 °C.

The SEM analysis of the precursors and the transformed crystalline powders obtained from reactions A–D reflect the consequences of the different reaction mechanisms in solution instrumental for the formation of the precursor itself. Thus the four different reactions exhibit differences in chemical composition and structure, in addition to the various particle sizes and their distributions (due to the competing rates of the formation of condensable species and their subsequent condensation reactions). These structural and compositional variations could provide different reaction pathways for the formation of the crystalline sulfide during the H_2S treatments. The contrast is clearly seen in the intermediate morphology of the powders for example, obtained from reactions A and B at 600 °C and at higher temperatures. The composition and structure allow different responses to the sulfur potentially leading to variations in the morphology of the product, which is clearly unique to the thio-sol–gel process. The heat treatment conditions can be used to control the defect structure and morphology of the TiS_2 powders, which in turn strongly influence the electrochemical properties of the material. These aspects are further discussed in the second part of this two-part series.

3.7 Synthesis of niobium disulfide

$Nb(OEt)_5$, plain (or unmodified) as well as modified with BSA (in a molar ratio of 1 : 10, acid to alkoxide) were separately dissolved in acetonitrile and reacted with H_2S at room temperature, causing the formation of a black precipitate. Chemical analysis of the precipitate (for Nb and S) is shown in Table 7. Infrared spectra collected on these precipitates in the range of 4000 to 200 cm^{-1} are shown in Fig. 11. Both spectra show the formation of Nb–S bonds as evidenced by the characteristic absorption at 357 cm^{-1}.[10] These bonds could have formed through a thiolysis–condensation mechanism similar to what was observed in the case of titanium. There are also unreplaced alkoxy groups in the precipitates as evidenced by the following absorptions (ref. 23, pp. 114–122; ref. 29): M—O stretching vibration at 585 cm^{-1}; terminal C—O vibrations at 925, 1264 and 1100 cm^{-1}; vibrations characteristic of the CH_3 group at 1376, 1440, 2872 and 2962 cm^{-1}; and vibrations characteristic of the CH_2 group at 1464, 2853 and 2926 cm^{-1}. In addition, the precipitate obtained from the modified alkoxide [Fig. 11(b)] shows additional absorptions at 1000 (sharp), 1020 and 1040 (shoulders) cm^{-1} which are characteristic of the sulfonyl group present in BSA.[29,30] From these observations, it is clear that the precipitates are formed by a partial thiolysis reaction of $Nb(OEt)_5$ with H_2S and condensation of the thiol groups, a mechanism similar to what has been determined in the case of titanium isopropoxide. In this case the extent of the condensation reaction has not been determined, but complete condensation is not expected due the five-fold coordination of Nb which could offer steric hindrance to condensation.

Table 7 Chemical analysis of precursors obtained by the reaction of niobium ethoxide with H_2S in acetonitrile

Reaction	Nb(wt.%)	S(wt.%)	S/Nb[a]
Plain alkoxide + H_2S in acetonitrile	43.6	29.6	2.0
Modified alkoxide + H_2S in acetonitrile	44.2	24.7	1.6

[a] Molar ratio of S to Nb.

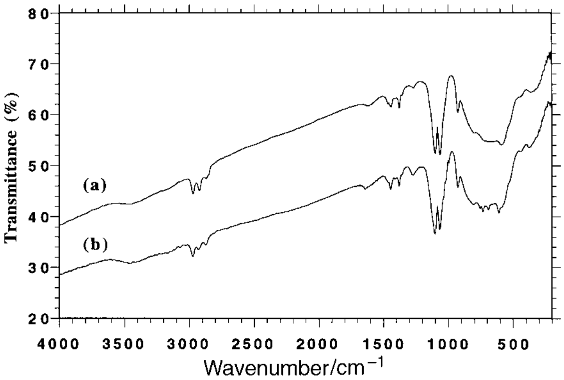


Fig. 11 IR spectra of precipitates obtained by the reaction of (a) $Nb(OEt)_5$ with H_2S in acetonitrile and (b) $Nb(OEt)_5$ modified with BSA reacted with H_2S in acetonitrile.

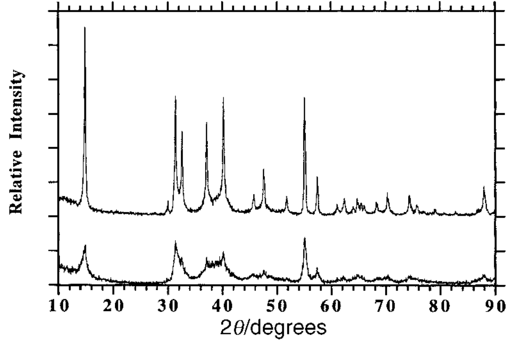
When the precipitates from both the reactions were heat treated in flowing H_2S at 700 and 800 °C for 6 h, they showed the formation of single phase NbS_2 (Fig. 12). At 700 °C, both powders show the presence of small crystallites of NbS_2.

SEM micrographs of the precipitates and the heat treated powders are shown in Fig. 13 and 14. In both cases, the precipitates consist of spherical particles ranging in size from 0.75 to 1 μm in diameter. At 700 °C, the powders derived from the modified alkoxide [Fig. 14(b)] clearly show a pseudomorphous transformation, causing the formation of NbS_2 platelets growing from the spherical particles. In the plain alkoxide derived powder, the platelets are not clearly distinguishable [Fig. 13(b)]. The particles have retained their spherical shape with increased roughness on the surface of the particles. At 800 °C [Fig. 13(c) and 14(c)], however, both powders show the presence of platelets ranging in size from a fraction of a micrometer to several micrometers. This is also approximately reflected in the extensive broadening at the base of the diffraction peaks in the XRD patterns obtained for the powders heat treated at 800 °C.

4 Summary and conclusions

The reaction of $Ti(OPr^i)_4$ with H_2S results in an alkoxysulfide precipitate through a thiolysis–condensation mechanism similar to the hydrolysis–condensation mechanism seen in the oxide-sol–gel process. The unique features of this reaction $\{Ti(OPr^i)_4 + H_2S\}$ are that the condensation reaction is rapid and all thiol groups that are bonded to titanium during the thiolysis of the isopropoxide condense to form Ti—S—Ti linkages in the solid.

Modification of the alkoxide by benzenesulfonic acid, the solvent system and the alkoxy group bonded to titanium all significantly influence the reaction of the alkoxide with H_2S. In the case of $Ti(OPr^i)_4$ modified with benzenesulfonic acid,


(a) Niobium ethoxide + H_2S

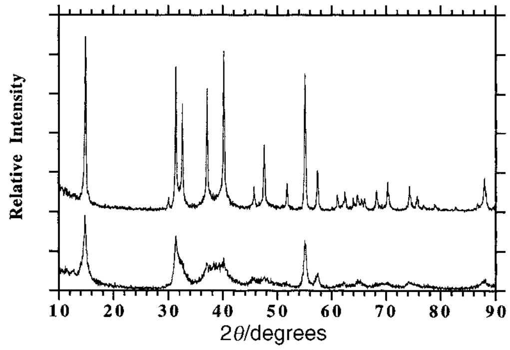

(b) Niobium ethoxide + BSA + H_2S

Fig. 12 X-Ray diffraction patterns of precipitates obtained by (a) the reaction of niobium ethoxide with H_2S in acetonitrile and (b) the reaction of niobium ethoxide modified with benzenesulfonic acid (in a molar ratio of $n=1:10$, acid to alkoxide), heat treated in flowing H_2S at 700 and 800 °C for 6 h respectively.

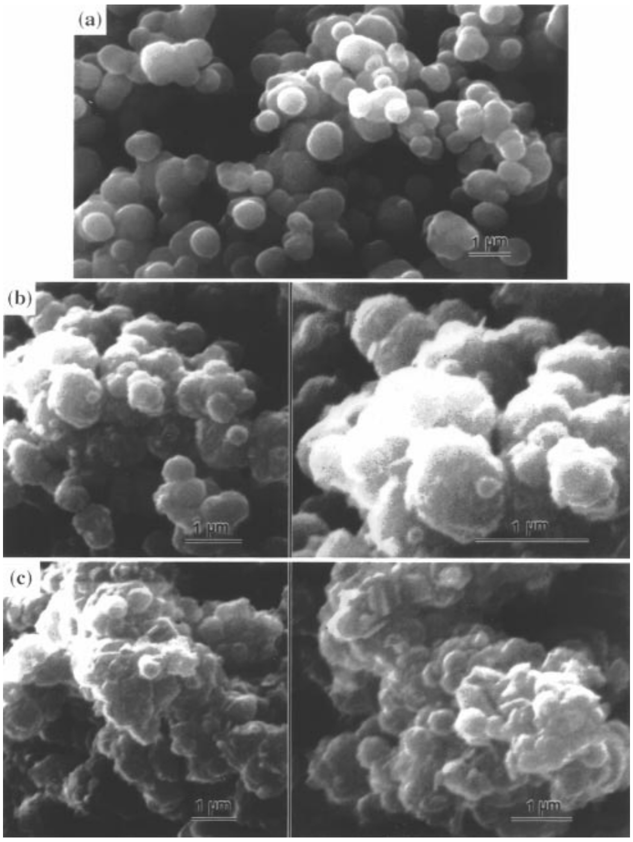


Fig. 13 SEM micrographs of (a) precipitates obtained by the reaction of niobium ethoxide with H_2S in acetonitrile, (b) the precipitate heat treated at 700 °C for 6 h in flowing H_2S and (c) the precipitate heat treated at 800 °C for 6 h in flowing H_2S.

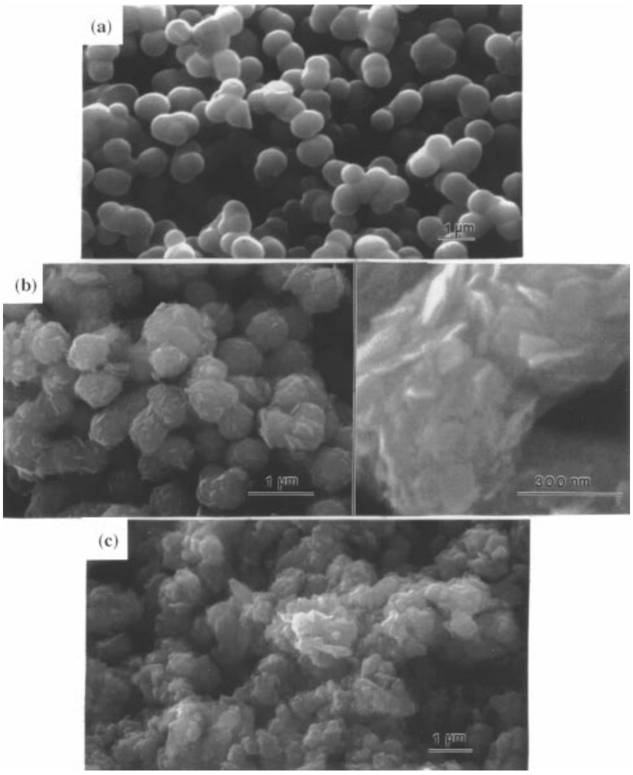


Fig. 14 SEM micrographs of (a) precipitates obtained by the reaction of modified niobium ethoxide with H_2S in acetonitrile, (b) the precipitates heat treated at 700 °C for 6 h in flowing H_2S and (c) the precipitates heat treated at 800 °C for 6 h in flowing H_2S.

chemical and spectroscopic analysis of the solid precipitate and of the liquid obtained from the reaction has revealed that the condensation reaction does not go to completion, possibly due to steric hindrance by the bulky benzenesulfonyl groups.

The solvent used for the reaction has a significant influence on the yield of the reaction. A comparison of the reaction of titanium isopropoxide and H_2S in different solvents has shown that acetonitrile is the best solvent system for the reaction because it facilitates the decomposition of H_2S to form highly nucleophilic SH^- species in solution. A comparison of the reaction of various alkoxides with H_2S has shown that steric hindrance plays a significant role in the reaction. Consequently, alkoxides with smaller alkoxy groups having lower molecular complexities in solution are more likely to undergo any significant thiolysis and condensation reactions with H_2S. Preliminary investigations have shown that the viscous liquid that forms from the reaction of titanium ethoxide with H_2S can be spin coated to form thin films. Titanium isopropoxide has also been reacted with dimethyldisulfide and hexamethyldisilthiane. Both reactions also lead to the formation of an alkoxysulfide precipitate although with a lower extent of sulfidization in comparison to H_2S.

All the reactions yield spherical alkoxysulfide precipitates that exhibit significant variations in particle size indicating differences in the rates of thiolysis and condensation reactions. Heat-treatment in flowing H_2S results in the formation of crystalline TiS_2 powder at different temperatures exhibiting striking variations in crystallite morphology. In particular, distinct differences can be observed between TiS_2 formed using plain $Ti(OPr^i)_4$ and that formed using $Ti(OPr^i)_4$ modified with benzenesulfonic acid. In the former, a wide platelet size distribution with random orientations have been observed. In the latter, a pseudomorphous transformation from the spherical precursor particles has been observed, leading to a platelet morphology which retains the overall spherical shape of the precursor particles.

Finally, the thio-sol–gel process has been used to synthesize NbS_2 in order to demonstrate the applicability of this process for the synthesis of other transition metal sulfides. In this system too, alkoxysulfide precipitates form, which can be converted to NbS_2 upon heat treatment in H_2S. NbS_2 synthesized by this method also exhibits variations in morphology similar to that observed in TiS_2.

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