A simple electrosynthesis route for preparation of nanocrystalline titanium sulphide film

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A variety of group IVB, VB, and VIB transition metal dichalcogenides have attracted considerable interest as reversible cathodes in ambient temperature secondary batteries because of their high diffusivity for alkali ions [1, 2]. Among the chalcogenides investigated as secondary lithium battery cathodes, the layered chalcogenide, TiS_2 has been identified and studied as an active cathode material in Li-based rechargeable batteries [3–6]. This is mainly because of high reversibility of lithium intercalation reaction, its good electronic conductivity, and high current capacity. The microstructure and morphology of the sulphide is extremely important, as the electrochemical performance of the sulphide is dependent to a large extent on the intercalation kinetics of lithium in to the cathode [7]. The battery performance of TiS_2 as a cathode can be improved if it can be synthesized in high purity with controlled morphology and optimum surface area [8].

Several methods to synthesis titanium sulphide powders have been reported. These methods can be divided into mainly high temperature and low temperature synthesis methods. The direct high temperature synthesis of titanium sulphide is based on the reaction of titanium metal and suphur at temperatures above 700 °C [8, 9]. The reaction requires long processing time and yields powders having a low surface area. Zehnder *et al.* [10] have used activated reactive evaporation process to deposit titanium sulphide thin films. Amorphous or poorly crystalline titanium sulphide has been prepared using low temperature synthesis methods. Amongst these, sol-gel, chemical precipitation and colloidal processing have received considerable attention. The ability to synthesize nanocrystalline fine particles at low temperature has also made these methods attractive for new materials with novel properties. The titanium sulphide powders have been produced using vapor phase reactions and chemical precipitation methods employing $TiCl_4$ as the starting material [11]. It has been known that titanium sulphide could be produced by the reaction between $TiCl_4$ and H_2S at temperatures greater than 400 °C. At low temperature $TiCl_4$ and H_2S does not interact. Bensalem *et al.* [12] have synthesized amorphous titanium sulphides by direct reactions between dry organic sulphurizing agents and $TiCl_4$. The crystalline phases of titanium sulphide were obtained by heating synthesized amorphous powders with sulphur.

There is technological interest in an efficient low cost material preparation technique for titanium sulphide. In the present work, for the first time, thin film of titanium sulphide has been deposited on ITO substrate by cathodic galvanostatic deposition from an aqueous alkaline solution containing complexed titanium. The process is conducted at room temperature and results in to nanocrystalline, compact, nonporous and uniform titanium sulphide film on ITO substrate. The deposition and characterization of titanium sulphide film are reported.

A room temperature (300 K) cathodic galvanostatic deposition of titanium sulphide film on ITO substrate has been carried out using following procedure. In brief, 0.05 M $TiCl_3$ solution was made by mixing $TiCl_3$ in conc. HCl in 1:2 ratio. To this, a solution of ammonium hydroxide (28%) was added with constant stirring. At pH about 10.0, a whitish-grayish precipitate was formed in the solution. This solution was filtered and used as stock solution as titanium source. The deposition bath was formed, by adding the equal amounts of titanium chloride from stock solution and 0.1 M thiourea solution in a beaker.

A platinum sheet with $1.5 \times 1.5\ \text{cm}^2$ area was used as the counter electrode. A scanning galvanostat/potentiostat (E G and G model-273A) was used in galvanostatic mode. A constant current of 0.5–2 mA/cm^2 was passed between ITO cathode and platinum anode. The deposition was carried out for time period of 30 min. After deposition, film was cleaned with triple distilled water and dried under argon flow. The film thickness of titanium sulphide film was estimated to be 0.1–0.5 micron.

Thin film of titanium sulphide was characterized using following techniques. The XRD pattern was obtained by using X-ray diffractrometer (RINT/PMAX 2500, Rigaku, Japan). Micro structural study was carried out with scanning electron micrographs, obtained with FE-SEM, (SM-6340F, JEOL, Japan). The optical absorption study was carried out with UV-VIS spectrometer (Varian cary 100, Australia). The charge storage capacity of titanium sulphide

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thin film in 1 M NaOH electrolyte was studied using a conventional three-electrode system using platinum counter electrode and Ag/AgCl reference electrode.

The reaction mechanism for electrodeposition of TiO_2, from acidic $TiCl_3$ solution under anodic bias, has been reported in the literature [13–15]. When the pH is less than 2.45, the solution contains the $Ti(OH)_2{}^{2+}$ species in $TiCl_3$ solution. However, if the pH is greater than 2.45, the $Ti(OH)_4$ species are present in the solution [13, 15]. The $Ti(OH)_4$ species are soluble in aqueous solution and remains soluble in bath in the alkaline pH region (pH > 7.0).

It is well known that thiourea hydrolyses in an alkaline medium to give sulphide ions as [16]

$$CH_3CSNH_2 + OH^- \rightarrow CH_3CONH_2 + S^{2-} \qquad (1)$$

The concentration of sulphide ions at cathode is sufficiently high to become associated with titanium ions as dissociated from the complexed pool of titanium ions to form titanium sulphide, which deposits on the cathode. The titanium is complexed with ammonia, which has stability constant of $10^{-9.8}$, reduces the concentration of free titanium ions. The pH of deposition bath is basic (>7), in which chemical equilibrium of complexing titanium ions shifts towards the associated complexed titanium ions. This minimizes the competitive reactions of titanium ions with hydroxide ions in the bath and any sulphide ions, which may be free in the bath. The alkaline pH of bath makes the hydroxyl ion concentration in such a way that the equilibrium involving the sulphide and hydroxide favors the sulphide ion as compared to the production of sulphide when the titanium ions exist in the solution complexed by ammonia. The electrodeposition of titanium sulphide takes place as per the follwing reaction mechanism.

$$x\mathrm{Ti(OH)}_4^+ + yS^{2-} + ze^- \Rightarrow \mathrm{Ti}_x\mathrm{S}_y \qquad (2)$$

Where x and y take different values corresponding to different titanium sulphide compounds.

TABLE I Comparison of observed "d" values with standard "d" values of titanium-sulphide compounds. (Peak positions correspond to Fig. 1 from the text)

Peak no.	Observed "d" value (A°)	I/Io (%)	Possible identification (Plane, compound, JCPDS card number)
1	4.1145	21	(115, $TiS_{1.5}$, 42-0772)
2	3.4715	13	(220, TiS_2, 36-1406)
3	2.9512	93	(220, TiS_2, 36-1406)
4	2.9360	100	(100, TiS_2, 15-0853), (101, Ti_2S_3, 40-1311), (009, TiS, 09-0289)
5	2.7233	44	(105,Ti_5S_8, 36-0532)
6	2.5433	39	(ITO), (107, TI_5S_8, 36-0532)
7	1.8038	26	(517, $Ti_{1.5}S$, 21-20772)
8	1.7945	32	(ITO)
9	1.5345	25	(410, Ti_5S_8, 36-0532)
10	1.5281	29	(ITO)
11	1.4618	12	(ITO)
12	1.3866	10	(ITO), (629, TiS_2, 36-1406)

The crystallinity of titanium sulphide film was analyzed using X-ray diffraction patterns. Fig. 1 shows a typical XRD pattern of titanium sulphide film on ITO substrate. The observed interplaner distance "d" values were compared with standard "d" values of titanium sulphide compounds, using JCPDS data cards. Table I shows this comparison. It is interesting to know that electrodeposited titanium sulphide consists of many non-stiochiometric compounds such as TiS, TiS_2, Ti_2S_3, $Ti_{1.5}S$, and Ti_5S_8. Bensalam and Schleich [12] have obtained different titanium sulphide phases (TiS_2, TiS_3 and Ti_3S_4), from amorphous powder, depending upon sulphur vapor pressure and heating temperatures. A few peaks corresponding to ITO substrate were observed. However, no peak corresponding to titanium oxide was detected in the XRD pattern. In general, amorphous to crystalline phase transition occurs at high temperature. We annealed titanium sulphide thin film samples at high temperature in air. However, single crystalline phase was not obtained up to 450 °C. Above 450 °C, the film thinning was observed [17]. However, such transition temperature, in case of titanium

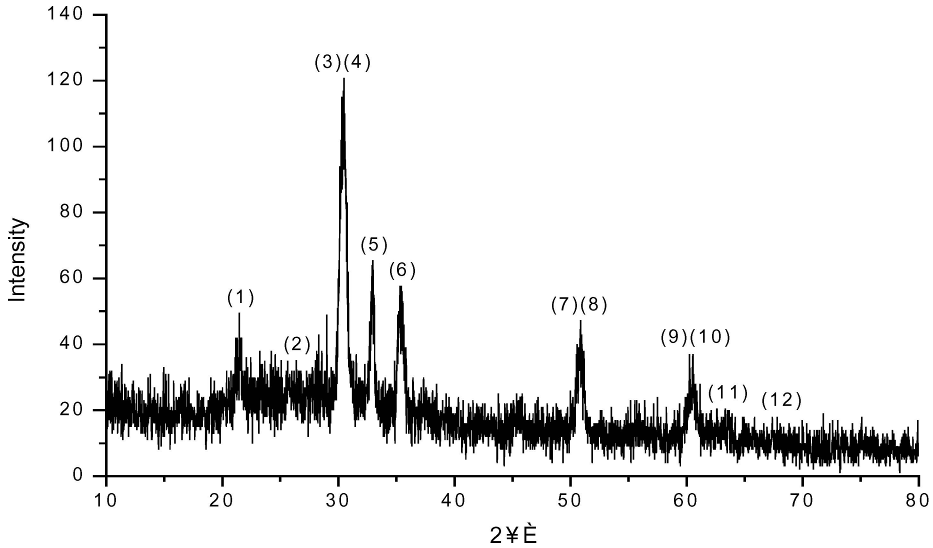
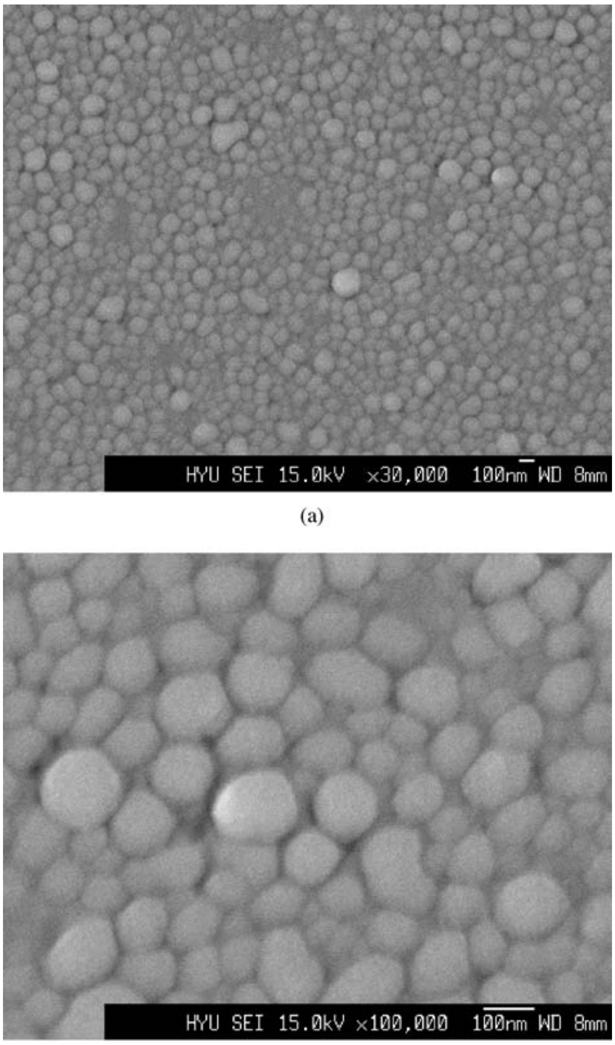


Figure 1 The X-ray diffraction pattern of titanium sulphide film deposited on indium doped tin oxide (ITO) coated glass.



(a)

(b)

Figure 2 The scanning electron microscopic (SEM) pictures at magnifications of (a) 30,000× and (b) 100,000× of titanium sulphide thin film deposited on ITO substrate.

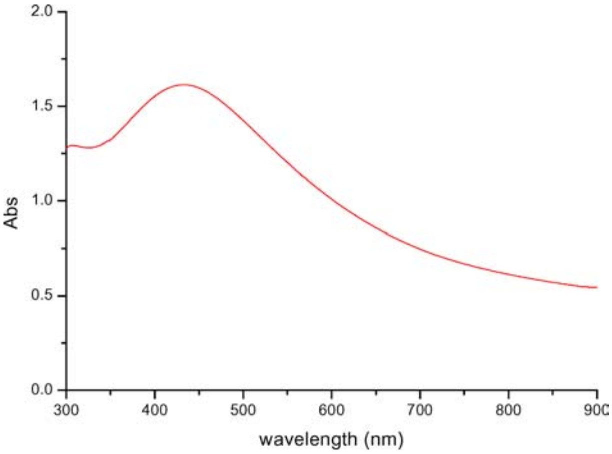


Figure 3 The optical absorption spectrum of titanium sulphide film deposited on ITO substrate.

sulphide powder, is reported to be preparative method dependent. For example, Sriram and Kumta [7] found that chemically precipitated titanium sulphide powders were amorphous and crystalline TiS_2 was obtained only after heating at 600 °C in H_2S atmosphere. However, Bensalem and Schleich [12] reported that amorphous titanium sulphide was transformed to crystalline TiS_2 above 200 °C heating in sulphur atmosphere and heating above 500 °C resulted in to liberation of sulphur and formation of non-stoichiometric TiS_2.

Scanning electron micrographs of titanium sulphide film on ITO substrate (Fig. 2a and b) at two magnifications (30,000× and 100,000×) were observed. A well covering, compact and non-porous titanium sulphide coating surface was observed at the magnification of 30,000×. At high magnification, elongated and round grains of 50–100 nm sizes are well seen. Sriram and Kumta [7] have observed spherical shaped morphology for amorphous powder obtained from titanium isopropoxide reacted with H_2S. However, the morphology was found to be dependent on temperature, feed gas, and pressure in case of MOCVD TiS_2 films [10]. The cross sectional view provided the information that the film is non porous and continuous. From cross sectional view of titanium sulphide film, a thickness is estimated to be 0.1 micron.

Fig. 3 shows variation of optical absorption with wavelength for titanium sulphide film. The optical absorption spectrum of titanium sulphide film on ITO coated glass showed a peak in absorption around 450-nanometer wavelength. The high optical absorption coefficient (10^4 cm^{-1}) indicates direct band gap transition. However, band estimation was not carried out as titanium sulphide film consists of many non-stoichiometric compounds.

In case of electrochemical supercapacitor, the capacitance comes mainly due to the pseudocapacitance of storage electrode by surface redox reactions between electrolytes and storage electrode [18–20]. The specific capacitance (F/g) is proportional to the specific surface area. Therefore, it is important to get more surface area of electrode material. It is demonstrated that amorphous or nanocrystalline form of electrode has a much higher specific capacitance than that of crystalline form [18].

The electrodeposited nanocrystalline titanium sulphide film was used in the formation of electrochemical supercapacitor and their performance was tested studying C-V curves. The C-V curves showed that voltametric current decreases with increasing sweep cycles and stable current is obtained after about 5 cycles. Fig. 4

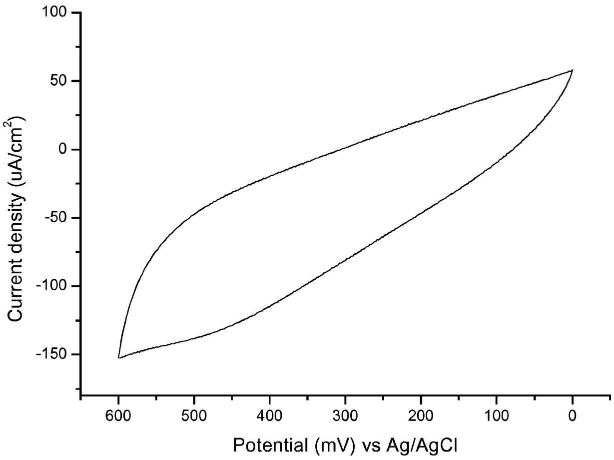


Figure 4 The cyclic voltammogram (C-V) of titanium sulphide film deposited ITO substrate in 1 M NaOH electrolyte. The scanning rate was 100 mV s^{-1}.

shows the C-V curve of titanium sulphide thin film at scanning rate of 100 mV/s. It is seen that voltametric current showed capacitive behavior. Only some broad peaks were obtained and the C-V curve is mainly featureless and indicates that this material can be useful as a capacitor electrode. The featureless curve is also indicative that the charge exchange between titanium sulphide and electrolyte is independent of voltage [18].

From this data, capacitance was calculated for titanium sulphide material deposited on ITO substrate, using following relation

$$C = I(\mathrm{A}) \big/ (\mathrm{dV} \big/ \mathrm{dt}) \tag{3}$$

Where,I is the average current in amphere and dV/dt is the voltage scanning rate (100 mVs^{-1}). The specific capacitance titanium sulphide was obtained by dividing its weight (0.36×10^{-4} g). The value of capacitance with deposited weight of titanium sulphide film showed the magnitude as high as 5 milli-farad cm^{-2} and specific capacitance as 140 F g^{-1}. The behavior showed that titanium sulphide electrode is stable in the NaOH electrolyte.

In conclusion, for the first time, simple electrosynthesis route has been used for the preparation of nanocrystalline titanium sulphide film using aqueous alkaline Ti(III)$\mathrm{Cl_3}$ solution. The film morphology is compact and consists of round grains between diameters of 50–100 nm. The titanium sulphide film showed absorption in visible region. Further, the cyclic voltammetry study showed the possibility of application of titanium sulphide film in energy storage devices.

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