

## **CHAPTER 3**

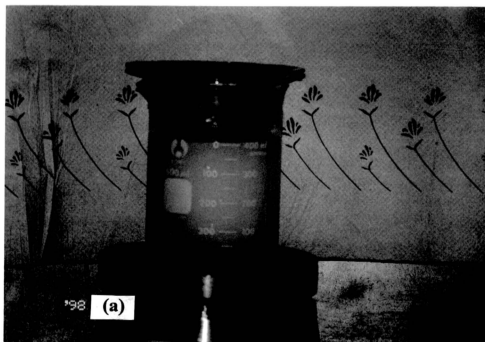
### **Synthesis and characterisation of tin dioxide and tin monoxide**

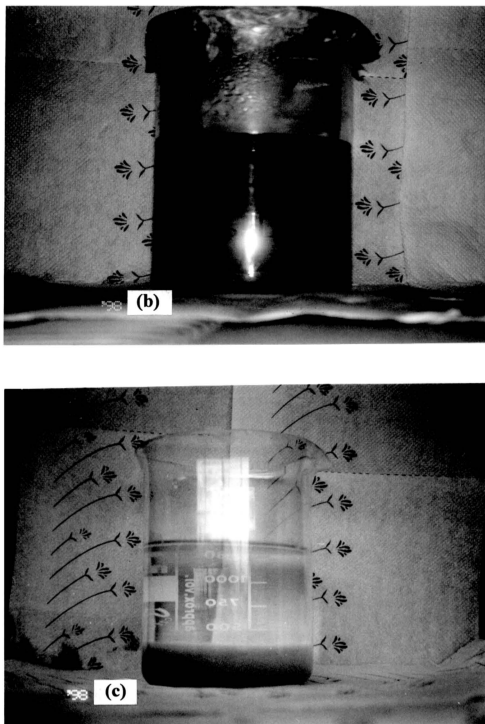
#### **3.1 Introduction**

The literature methods for preparing tin oxide make use of the sol-gel and co-precipitation methods (Miyata *et al*, 1997; Senguttuvan and Malhotra, 1997; Lane, 1984; Kudryartseva *et al*, 1997; Fuller and Arwick, 1974). A quantity of tin tetrachloride hydrate was dissolved in distilled water, and to this solution ammonium hydroxide was added. Variations of this method include mixing an alkali metal stannate with a suitable acidic precipitating agent (Kudryartseva *et al* 1997), dissolving metallic tin in nitric acid and heating the resulting hydrous stannic oxide with a quaternary ammonium hydroxide; hydrolysis of tin oxide under basic conditions; (Segal *et al*, 1985) and pyrolysis of an aerosol produced by ultrahigh frequency spraying of tin chloride solution in a tubular furnace (Gulliver *et al*, 1991; Cabanes *et al*, 1992). In the present work, the preparation of tin dioxide following the method given in the literature (Vallet-Regi *et al*, 1993; Radhakrishna, 1997), and using only tin dichloride solution as the starting material, are described. The tin dioxide obtained has been characterised and the factors that influence the synthesis were studied.

### 3.2 Synthesis of tin dioxide

10 g of tin(II) dichloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) was dissolved in 1.5 L water to give a white mixture as shown in Fig. (3.1, a). This mixture was then subjected to stirring for 48 hours during which time the mixture turned cloudy and then yellow. The mixture was acidic, as suggested by its pH. A clear yellow solution was obtained on filtering the mixture as shown in Fig. (3.1, b). The solid residue was removed. After several days keeping the yellow solution at room temperature, a yellow gel was formed Fig. (3.1, c). The gel settled on the bottom of the beaker; the supernatant water was decanted. The gel was washed repeatedly with distilled water to remove chloride ions. When left in water for several weeks, the yellow gel turned white.





**Fig. (3.1):** (a) whitish mixture upon mixing of reacting materials, (b) yellow solution obtained after filtration of mixture after 48 hours of stirring (c) gelation of the solution after two weeks

### 3.3 Factors influencing the gel formation

Three factors appear to affect the formation of tin dioxide gel: the concentration of tin dichloride, the temperature of the reaction and the reaction time.

#### 3.3.1 Concentration of tin dichloride in water

Solutions of different concentrations of tin dichloride were prepared and stirred for the same length of time at room temperature. The results, presented in Table. (3.1), shows that the gelation time depends on the concentration of tin in water.

Table (3.1): Variation of concentration of tin dichloride with time for gelation of tin dioxide

Concentration of $\text{SnO}_2$ in water	Time needed for gelation
10 g.L <sup>-1</sup> $\text{SnCl}_2$	15 Days
5 g. L <sup>-1</sup> $\text{SnCl}_2$	10 Days
1 g. L <sup>-1</sup> $\text{SnCl}_2$	1 Day
0.5 g. L <sup>-1</sup> $\text{SnCl}_2$	0.5 Day
0.2 g. L <sup>-1</sup> $\text{SnCl}_2$	Few minutes

The results are also presented as a plot in Fig. (3.2). The  $x$ -axis is the concentration of the tin dichloride solution and the  $y$ -axis the time needed for the gelation of the tin dioxide.

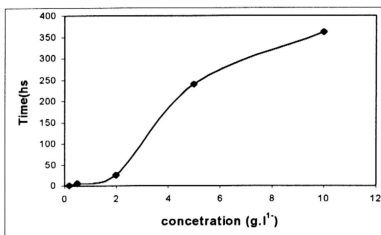


Fig. (3.2): Graph of the concentration of tin dichloride *versus* time of gelation of tin dioxide.

### 3.3.2 Temperature of reaction

Solutions of tin dichloride of the same concentration ( $3 \text{ g L}^{-1}$ ) were stirred for the same length; the temperature of the solutions were varied from  $30^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ . The results are summarised in Table (3.2).

Table (3.2): Temperature and time needed for gelation.

Solution	Temperature ( $^{\circ}\text{C}$ )	Gelation time
<b>A</b>	30	10 days
<b>B</b>	40	3 days
<b>C</b>	60	0.25 day
<b>D</b>	80	Few minutes
<b>E</b>	100	Few minutes

Fig. (3.3) shows the approximate asymptotic relationship between temperature of the solution and gelation time. The solution kept at room

temperature shows a longer time for gelation whereas the solution that had been boiled shows rapid gelation.

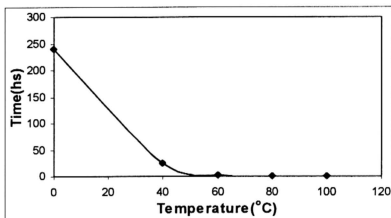


Fig. (3.3): Graph of the temperature of the solution and time of gelation of tin dioxide.

### 3.3.3 Stirring time

As the physical nature of the tin dichloride determines its solubility in water, the stirring time and its effect on gelation was further investigated. In this experiment, a solution of known concentration was stirred at room temperature overnight; the acidity of the solution was then monitored by using a pH meter. The results are presented in Table (3.3) and Fig. (3.4).

Table (3.4): Stirring time and pH value

pH	Time (hr)	pH	Time (hr)	pH	Time (hr)
6.5	0.01	1.4	10	1.4	20
1.9	1	1.4	11	1.4	21
1.6	2	1.4	12	1.4	22
1.6	3	1.4	13	1.4	23
1.5	4	1.4	13	1.4	24
1.5	5	1.4	14	1.4	25
1.4	6	1.4	15	1.3	25
1.4	7	1.4	16	1.3	30
1.4	8	1.4	17		
1.4	9	1.4	19		

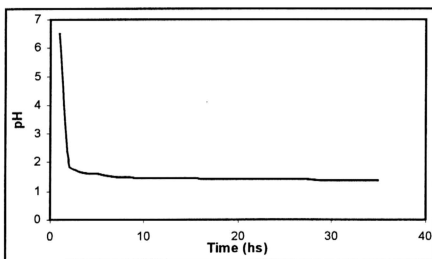


Fig. (3.4): Graph of pH value variation with stirring time.

### **3.4 Characterisation of tin dioxide**

#### **3.4.1 X-ray diffraction**

The XRD pattern of the white and yellow gel is given in Fig. (3.5). The pattern is almost similar to each other. Upon comparing with the JCPDS data, the gels are semi-amorphous phases of tin dioxide.

Fig. (3.6) depicts the X-ray diffractogram of the gel dried at room temperature. The peaks in the XRD pattern are characteristic of a semi-amorphous solid being broad and of low intensity. A broad peak is observed at  $15^\circ$  and other more crystalline peaks are observed at  $\sim 27^\circ$ ,  $33^\circ$ ,  $37^\circ$ ,  $52^\circ$  and between  $60^\circ$  and  $65^\circ$ . Peaks above  $70^\circ$  are not quite distinct. Upon comparison with the JCPDS data, it can be inferred that the gel is semi-amorphous tin dioxide. When the gel is heated to  $500^\circ\text{C}$  and  $800^\circ\text{C}$ , the XRD patterns show a more defined crystalline structure and the X-ray diffraction peaks match well with those of the JCPDS: 41-1445 standard.



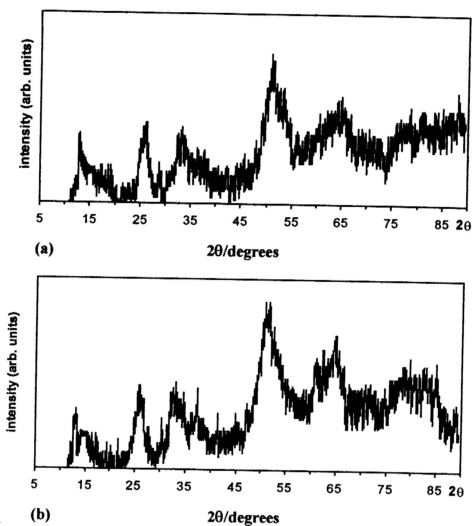


Fig. (3.5): XRD pattern of (a) white gel and (b) yellow gel.

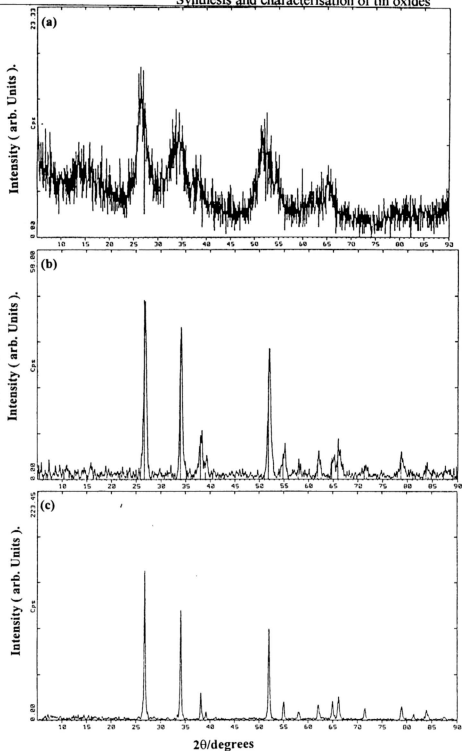


Fig. (3.6): XRD pattern of gel dried at (a) room temperature, (b) 500°C, superimposed with reference data (JCPDS: 41-1445), (c) 800°C.

### 3.4.2 Thermal analysis

Fig. (3.8) shows the thermograms from the DSC, DTA and TGA measurements. Both the DSC and DTA plots Fig. (3.8, a,b) do not show any crests. As sharp crests are associated with a change of phase of the material under study, the absence of such crests in Fig. (3.8) suggests that the tin dioxide gel is not amorphous (i.e., it is, in fact, semi-crystalline). The crystallinity is supported by the X-ray diffractogram in Fig. (3.5) and (3.6). The TGA plot Fig. (3.8, c) implies that the as-prepared tin dioxide contains approximately 1.5 molecules  $\text{H}_2\text{O}$  for each formula unit of tin dioxide.

The DSC and DTA curves show only a valley at about  $90^\circ\text{C}$  that corresponds to the loss of water. The TGA plot shows that the rapid loss of weight at  $90^\circ\text{C}$  confirming the loss of water, weight loss continue but on a gradual manner until  $550^\circ\text{C}$ , when the compound has reached stability. The gradual loss in weight is probably due to left over chlorides used during the preparation of the tin dioxide.

From TGA graph Fig. (3.8, c), 16% weight loss attributed to water was noted. This is because the weight loss occurs at around  $100^\circ\text{C}$ . By assuming that the final product is  $\text{SnO}_2$ , the molecular weight of which is 150.69, then this represents 84% of the initial product which is again assumed to be  $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ . By simple calculation  $x = 1.6$ .

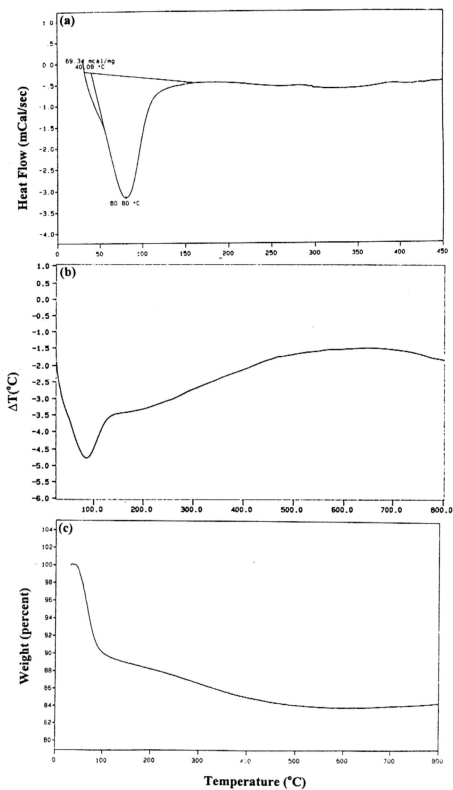
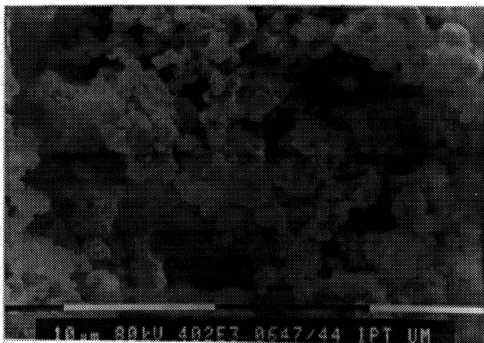


Fig. (3.8): Thermal analysis of tin dioxide (a) DSC, (b) DTA and (c) TGA.

### 3.4.3 SEM photographs of the gel

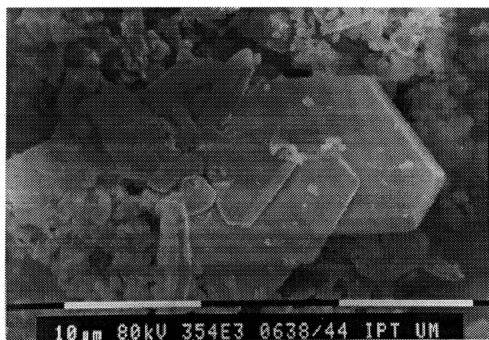
Fig. (3.9) shows the SEM photographs of tin dioxide that had been heated at 500°C and 800 °C. The photograph of the sample of the gel material dioxide that has been dried at room temperature shows agglomerates of small particles. The photograph of the sample heated at 500 °C and 800°C shows an increase in particle size and the material appears to be somewhat more crystalline, as noted from the previous X-ray diffractogram Fig. (3.6).



(a)

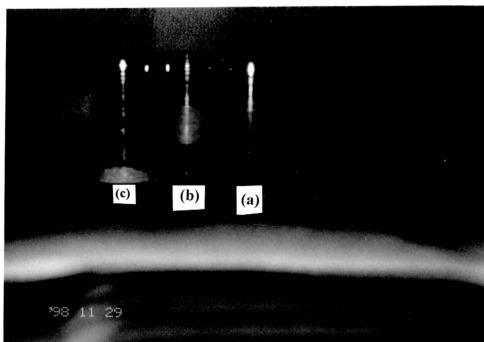


(b)



(c)

Fig. (3.9): SEM micrographs of (a) the yellow gel dried at room temperature and (b) dried at 500 °C, (c) dried at 800 °C



**Fig. (3.10):** Photograph of the gel tin dioxide at:  
(a) room temperature heated to (b) 500°C, (c) 800°C

### 3.4.4 Fourier Transform Infrared spectroscopy

FTIR was used to investigate the compound in the 400-4000  $\text{cm}^{-1}$  wavenumber range. The room temperature sample shows an intense, broad band at 3400  $\text{cm}^{-1}$  Fig. (3.11) that is characteristic of water. The band corresponds to the O-H stretching mode.

A broad band at about 600  $\text{cm}^{-1}$  is assigned to the Sn-O stretching. At 500°C, a new band appears at around 500  $\text{cm}^{-1}$ , and at 800°C, bands appear at around 700 and 420  $\text{cm}^{-1}$ . These results are in agreement with (Ocaña *et al.*, 1993).



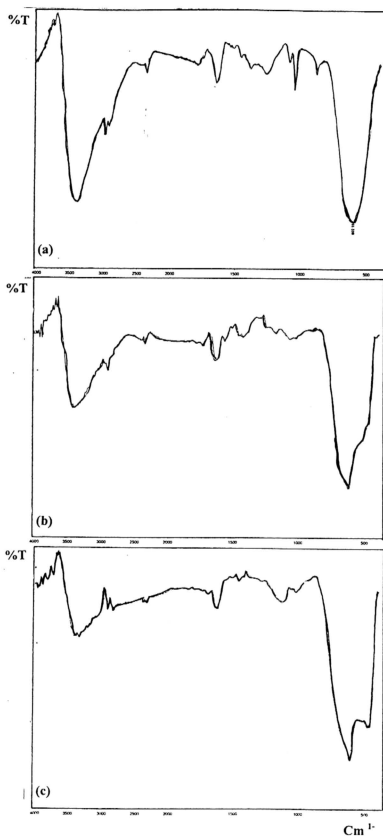
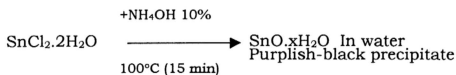


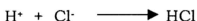
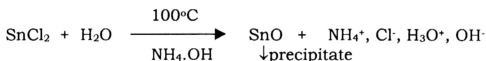
Fig. (3.11): FTIR spectra of tin dioxide at:  
(a) room temperature, (b) 500°C, (c) 800°C

Tin monoxide is a purple-black compound; it has a layered structure similar to that of lead (II) oxide (Choi *et al*, 1997). An aqueous solution of tin dichloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) was heated until boiling for fifteen minutes. To the hot faint-yellow solution ammonium hydroxide solution ( $\text{NH}_4\text{OH}$  10%) was added. A purplish-black solid precipitate was obtained. The mixture was cooled; the supernatant liquid decanted and the solid was washed with water several times. The product was then air-dried. The steps involved are shown below:



### 3.6 Factors influencing the preparation of tin monoxide

The stirring time, temperature and the amount of 10% aqueous ammonium hydroxide were found to be the factors that influence the preparation of tin monoxide.



### 3.6.1 Stirring time

When the solution of tin dichloride is boiled, stirring for more than 15 minutes produces tin dioxide instead of tin monoxide.

### 3.6.2 Temperature

The solution has to be heated to 100°C to ensure good yields of tin monoxide. A lower temperature results in the formation of a large quantity of tin dioxide.

### 3.6.3 Ammonium hydroxide

An adequate (3 cm<sup>2</sup>) amount of ammonium hydroxide (NH<sub>4</sub>OH 10%) was added to the boiling solution of tin dichloride (6 gL<sup>-1</sup>). After five minutes the colour of the solution changed from yellow to purplish black, and this was followed by the precipitation of tin monoxide.

### **3.7 Characterisation of tin monoxide**

#### **3.7.1 X-ray Diffraction**

Fig. (3.12) depicts the X-ray diffractogram of the as-prepared tin monoxide. The X-ray diffraction peaks match well with those of the JCPDS:6-0395 standard. The sharpness of the peaks implies that the tin monoxide obtained by this method exists in a crystalline state.

Generally, inorganic compounds that are prepared by using soft chemistry techniques are amorphous or semi-amorphous compounds, as exemplified by vanadium oxide (Znaidi *et al.*, 1989) and tin dioxide. For the tin monoxide, a high degree of crystallinity is achieved with further heat treatment.

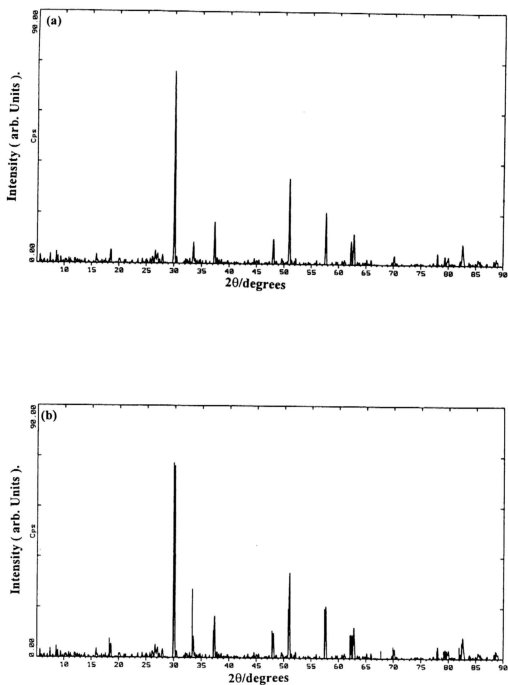


Fig. (3.12): XRD pattern of (a) tin monoxide (b) tin monoxide superimposed with the reference (JCPDS:6-0395).

### 3.7.2 Thermal analysis

Fig. (3.13) shows the DTA thermogram under air and the TGA thermogram under nitrogen gas. The TGA thermogram shows two losses of water, the first at about 100°C (which corresponds to the loss of lattice water) and the second at about 300°C (which probably corresponds to the loss of coordinated water). The number of water molecules that are present at room temperature in tin monoxide is calculated to be approximately nine.

The DTA thermogram shows a valley around 100°C; the valley corroborates the loss of lattice water that is implied by the TGA. A broad crest at about 170°C is interpreted in terms of the oxidation of tin monoxide to tin dioxide.

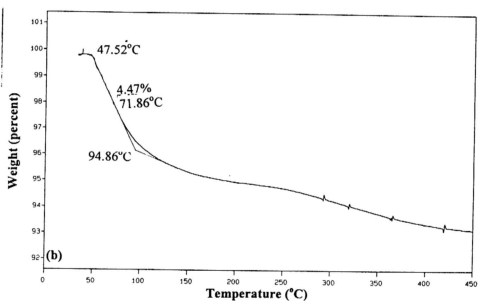
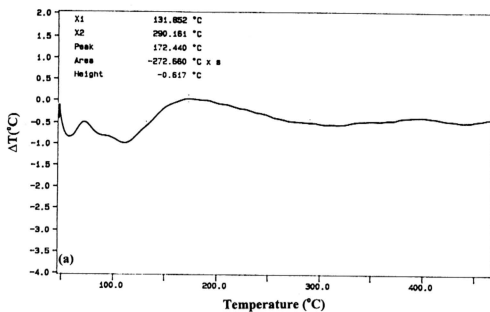


Fig. (3.13): Thermal analysis of tin monoxide (a) DTA, (b) TGA

### 3.7.3 SEM Photographs of tin monoxide

Fig. (3.14) shows the photographs of the as-prepared tin monoxide under the scanning electron microscope. The particles are larger than  $1\mu\text{m}$ , and are assembled in different places as a possible consequence of the high degree of crystallinity.

The size of the particle is related to crystallinity of the compound, and small particles generally show low crystallinity whereas big particles size show good crystallinity. In comparison, tin dioxide presents only small particles, and it is therefore of low crystallinity.

### 3.7.4 Transformation from tin monoxide to tin dioxide

Fig. (3.15) and Fig. (3.16) depict the X-ray diffractograms and the IR spectra of the product obtained when tin monoxide is heated at  $500^{\circ}\text{C}$  and at  $800^{\circ}\text{C}$ . The product is identified as tin dioxide by comparing its diffractogram with that of the standard sample JCPDS: 41-1445. The IR spectrum of tin dioxide is almost identical to that of tin monoxide. The DTA plot in Fig. (3.13) suggests that the oxidation of tin monoxide occur at a relatively low temperature ( $170^{\circ}\text{C}$ ). To probe the room-temperature oxidation of the compound, tin monoxide was kept in water for three weeks. Fig. (3.17) shows the SEM photograph of the sample at the end of this period. The photograph shows a morphology that is different from that of the sample Fig. (3.14).



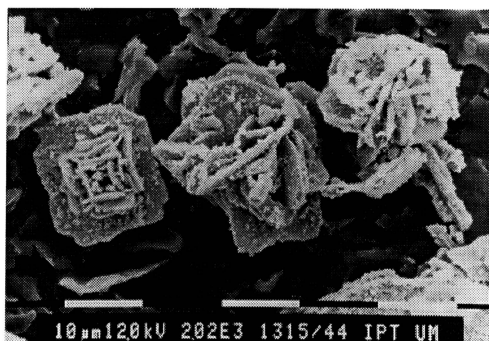


Fig. (3.14): SEM micrograph of tin monoxide at room temperature

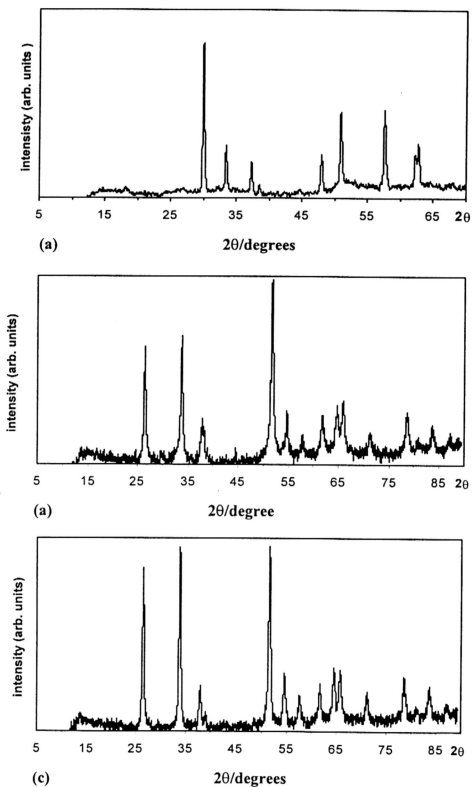


Fig. (3.15): XRD pattern of tin monoxide at:  
(a) room temperature, (b) 500°C, (c) 800°C.

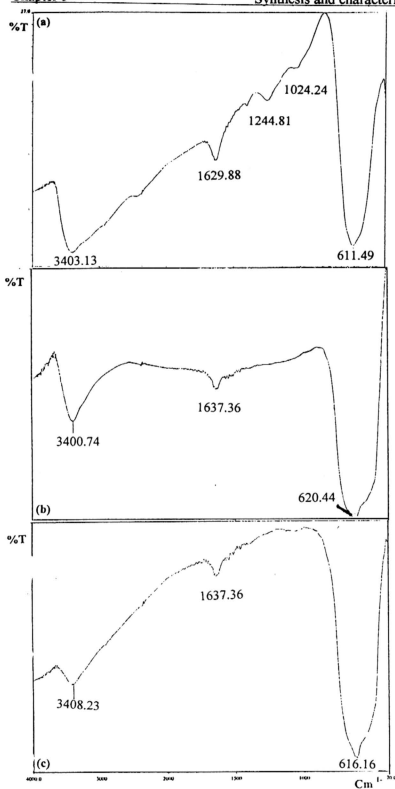


Fig. (3.16): FTIR spectra of tin monoxide at:  
(a) room temperature, (b) 500°C, (c) 800°C

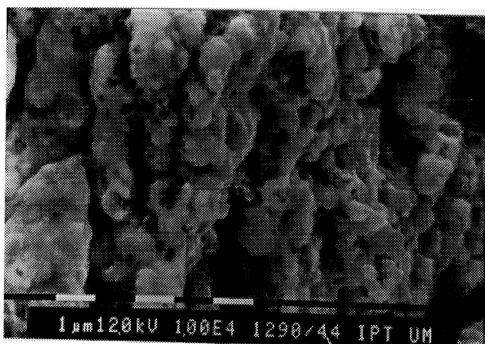


Fig. (3.17): SEM micrograph of tin monoxide in water for three weeks