Chapter 2: Aqueous Sol-gel Synthesis of Nanocrystalline Titania from Titanyl Sulphate

2.1 Abstract

An aqueous sol-gel method based on hydrolysis-peptisation has been developed for the preparation of nanocrystalline titania using titanyl sulphate as precursor. The stability of the sol has been monitored using the zeta potential measurement. The sol has been stabilized in acidic and basic pH range. A stable titania sol with extremely narrow range of distribution of particles having an average size of 27 nm has been obtained at a pH range 1.8 to 2.2. Thermo gravimetric and differential thermal analyses were used for the characterisation of the sol-gel derived titania powder. X-ray diffraction analysis has been used for the phase identification of the titania sample heated at different temperatures. The crystalline anatase particles have average particle size of 12–32 nm and specific surface area of 48.7–6.5 m²g⁻¹ between the calcination temperature 500–700 °C. The type IV isotherm indicates the mesoporous nature of the powder obtained through the present method. Transmission electron microscope image indicates that titania obtained through the present method after calcining at 600 °C have a crystallite size of 23 nm.

2.2 Introduction

Nanocrystalline anatase titania becomes increasingly important because of its potential application in catalysis/photocatalysis, coating for self-cleaning surfaces, ceramic membranes and sensors.¹⁻⁴ Crystalline structure, particle size, surface area, porosity, thermal stability and morphology of the titania determine their efficiency in
vivid applications. In developing novel catalytic/photocatalytic systems, it is essential to develop a titania with possible higher surface area or equivalently, the smallest particle size.\textsuperscript{5} Sol–gel method has become one of the successful and simple technique for preparing nanosized titania.\textsuperscript{6} Most of the earlier attempts used titanium alkoxides as precursors in the sol–gel route. The novel approach to start from titanyl sulphate (TiOSO\textsubscript{4}) or chloride (TiCl\textsubscript{4}) followed by peptisation through aqueous medium to the pure anatase phase appears to be very interesting. In 1998, Tsevis et al.\textsuperscript{7} investigated the preparation and characterisation of anatase powder starting from TiOSO\textsubscript{4} by hydrolysis with KOH and they obtained relatively high surface area ranging from 135 to 250 m\textsuperscript{2}g\textsuperscript{-1} but the method leads to preparation of bulk powders. Titania particles where prepared by controlling the hydrolysis conditions of the precursor and by using different catalysts. They were then characterized by X-ray diffraction and hence the structural parameters, concentration of anatase-rutile phases and average crystal size of titania were obtained.\textsuperscript{8} Titania particles of submicron size have been prepared by aging a highly acidic solution of TiCl\textsubscript{4} at 95 °C by using sulphate ion as control agent.\textsuperscript{9} Controlled hydrolysis of TiCl\textsubscript{4} below 0 °C resulted in nanosized anatase, but failed to hold the reproducibility of the anatase particle size.\textsuperscript{10} Li et al.\textsuperscript{11} reported a novel method for the preparation of nanocrystalline rutile titania powders by liquid hydrolysis of TiCl\textsubscript{4}. The nanocrystalline nature of titania obtained by sol-gel method was examined using HRTEM, BET surface area analysis and XRD techniques\textsuperscript{12} and found that the specific surface area from its intial value of 169 m\textsuperscript{2}g\textsuperscript{-1} at low temperature calcination of the gel got reduced to 2.7 m\textsuperscript{2}g\textsuperscript{-1} at 983K. The size of anatase crystallite changed from 4.5 to 6.5 nm. Studies based on electron microscopy and atomic force microscopy indicate that the size of titania also
depends on temperature of processing. In the range 290K to 820K, the titania grains consisted of anatase and brookite phase. High resolution electron microscopy showed that sample gel heated to 573 K had grain sizes in the range of 4.5-7 nm which increased to 7-12 nm with an average of 9 nm when heated to 820 K and had pore sizes between 6-10 nm. Possibility of obtaining rutile form of titania was also reported starting from titanyl salts. Park et al. reported thermal hydrolysis of Ti(SO₄)₂ at 80 °C in a mixed solvent of n-propyl alcohol and water. The as precipitated powder was amorphous hydrates of titania and were crystallised by calcination into anatase (>600 °C) and rutile (>800 °C). Wei et al. prepared nanodispersed spherical TiO₂ powder, of average particle size of 80 nm, by forced hydrolysis of Ti(SO₄)₂ aqueous solution containing sulfuric acid under boiling reflux condition. Iwasaki et al. synthesized nanocrystalline anatase by thermal hydrolysis of titanylsulphate in a mixed solution of alcohol and water. The size of the anatase crystallites was controlled between 2 and 7 nm, by adjusting the preparation conditions such as water/alcohol ratio and reflux time. The powder after calcinations at 400 °C had a specific surface area of 68 m²g⁻¹, which reduced to 30 m²g⁻¹ on further calcination at 600 °C. Earlier, Kato et al. reported the formation of spherical TiO₂ powders from an aqueous solution of titanyl sulfate by homogeneous precipitation using urea as the precipitating agent and claimed the essential presence of urea for obtaining spherical particles. Recently, the photoactivity of titania derived from titanylsulphate by thermal hydrolysis and precipitation has been reported, but these methods lead to bulk titania powders. In this chapter we presented a new aqueous sol-gel method for the synthesis of nanosized anatase titania by homogeneous precipitation of titanyl sulphate.
solution at room temperature. This method is useful for preparation of photoactive nanopowder, dense and porous coatings as well as photoactive nanodispersions.

2.3 Experimental

Titanyl sulphate (Aldrich Chemicals, 99.99 % purity) was dissolved in 500 ml of doubly distilled water (0.2 M) and was subjected to precipitation by the slow addition of ammonium hydroxide (sd Fine chemicals, 25%, India Ltd) solution under constant stirring at room temperature (32 °C). The hydrolysis was controlled with the addition of NH₄OH (sd Fine chemicals, 25%, India Ltd), until the reaction mixture attains a pH 8.5. The precipitate obtained was separated by filtration, and washed repeatedly with distilled water until the precipitate becomes free of sulfate ion (confirmed by BaCl₂ test). The peptisation of the precipitate was done by dispersing the precipitate in 1000 ml of hot distilled water by adjusting the pH in the acidic and basic range using HNO₃ (GR Merck, 69%, India Ltd) and Ammonia (sd Fine chemicals, 25%, India Ltd) solution respectively. Stability of the sol was followed by zeta potential measurement at different pH values using Malvern Zetasizer 3000HS (U.K). Sol particle size distribution was analysed by Malvern 3000 HS (U.K) particle size analyser. The sol to gel conversion was achieved by drying the sol in a water bath. The gel was again dried at 70 °C in an oven over a period of 24h. Thermal analysis of the gel was carried out in flowing nitrogen gas at a heating rate of 10 °C min⁻¹ in Shimadzu TG /DT 50H thermal analyzer. The dried gel was then calcined at 500, 600, 700, 800 and 850 °C in separate batches for 1h with a heating rate of 10 °C min⁻¹. The flow chart for the preparation for stable titania sol is provided in Figure 2.1.
The gel and the calcined powders were characterised by powder X-ray diffraction, thermal analysis and N\textsubscript{2} adsorption surface area analysis. XRD patterns were obtained with a Philips PW 1710 diffractometer, using Ni-filtered Cu K\textalpha{} radiation, and the crystallite size was calculated using Scherrer formula as given in equation 2.1.\textsuperscript{24}

\[
\Phi = \frac{K\lambda}{\beta \cos \theta}
\]  

(2.1)

where $K$ is the shape factor taken as 0.9 for the calculations presented, $\lambda$ the wavelength of the X-ray, $\beta$ the full width at half maxima, and $\theta$ the diffracting angle.

Figure 2.1. Flow chart for the preparation of titania sol
The rutile fraction in the sample was determined by measuring the XRD intensities of anatase (101) and rutile (110) from the equation 2.2.25

\[ W_R = \frac{1}{1 + 0.8(I_A/I_R)} \]  

where \( W_R \) is the weight fraction of the rutile present, \( I_A \) and \( I_R \) are the X-ray integrated intensities of anatase 101 plane and rutile 110 plane respectively. IR spectra were recorded in a Nicolet Magna 560, FTIR spectrometer in the range 400-4000 cm\(^{-1}\) on powders dispersed in KBr pellets. Surface area and pore analysis of the samples were carried out by N\(_2\) adsorption in a Micromeritics Gemini 2375 surface area analyzer after degassing the samples at 200 °C for 2h. The TEM observation of the calcined titania powder was performed on a Hitachi HF 2200 TU field emission microscope operating at an accelerating voltage of 200 kV.

2.4 Results and Discussion

2.4.1 Zeta Potential, particle size Vs pH of the sol

Most particles dispersed in an aqueous system will acquire a surface charge, principally either by ionization of surface groups, or adsorption of charged species. These surface charges modify the distribution of the surrounding ions, resulting in a layer around the particle that is different from the bulk solution. If the particle moves, under Brownian motion, this layer also moves as part of the particle. The zeta potential is the potential at point in this layer where it moves past the bulk solution. This is usually called the slipping plane. The charge at this plane will be very sensitive to the concentration and type of ions in solution. A schematic representation of the origin of zeta potential is given in Figure 2.2. Zeta potential is one of the main forces that mediate interparticle interactions. Particles with a high zeta potential of the same charge sign,
either positive or negative, will repel each other. Conventionally a high zeta potential can be high in a positive or negative sense, i.e., <-30mV and >+30mV would both be considered as high zeta potentials. For molecules and particles that are small enough, and of low enough density to remain in suspension, a high zeta potential will confer stability, i.e. the solution or dispersion will resist aggregation. So zeta potential is the measure of stability of colloidal particle in the suspension.

Zeta potential and particle size against pH of titania particle was given in the Figure 2.3. It shows that at lower pH below 2.5 and higher pH above 7.5 the particle shows a zeta potential value above ± 30mV which indicates that the peptisation of the particle below pH 2.5 and above pH 7.5 may leads to stable colloid. From these observations we can conclude that at lower pH, the preferential absorption of H⁺ ion on to
the surface of the titania particle from HNO₃ (used for peptisation) increases the surface charges and makes the particles repel each other and stay apart, i.e., the electrostatic stabilization occur. The zeta potential value indicates that the preferential adsorption of ions on the surface of the particles increases the zeta potential value above +30 mV. The same phenomena happened in the higher pH range also, where the preferential absorption of hydroxyl species from ammonium hydroxide (used for peptisation) on the surface increases the zeta potential value in the negative region. Zeta potential value between pH 2.5 to 7.5 also shows a value between +30 mV and -30 mV. The particle size number also indicates that in the pH range 2.5 to 7.5, the particles are aggregated, which is due to lowering of surface charge in this region which makes the particles to come closer to each other and aggregate. The average particle size increases from 27 nm obtained at pH 2 to 490 nm at pH 3 which further increases to 1250 nm at pH 6.5. However at pH 8.5 the average particle size has a value of 130 nm. The particle size distribution is given in Figure 2.4. It indicates that in the pH range 2.5 to 7.5, the surface charge is not enough to keep the particle apart.

![Figure 2.3.](image)

**Figure 2.3.** Zeta potential and particle size of titania colloids as a function of pH.
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Figure 2.4. Particle size distribution curve of titania at (a) pH 2 (b) pH 3 (c) pH 6.5 and (d) pH 8.5.

The photograph of the titania nanoparticles peptised at different pH is given in Figure 2.5. From this photograph we can see that in between pH 2.5 and 7.5 the titania particles gets aggregated and settle down.

Figure 2.5. Photograph of the titania nanoparticles peptised at different pH (i) 2 (ii) 2.5 (iii) 4.5 (iv) 7.5 (v) 8.5
For further studies, the region related to lowest particle size which is at pH 2, was selected for the peptisation of particle. A monomodal distribution of particles was obtained at pH 2 with an average particle size of 27 nm as provided in Figure 2.6a. The particle size distribution of titania sol aged for six months is also provided in Figure 2.6.

**Figure 2.6.** Particle size distribution curve of titania sol (a) at pH 2 (b) aged for six months and (c) aged for six months after ultrasonication for 10 min.

We could not observe any visible sedimentation or flocculation even after keeping the sol for six months. There was, however, a very slow tendency for the sol particles to undergo particle growth resulting in a slightly higher monomodal distribution of average size of about 32.7 nm (Figure 2.6). When this sol was ultrasonicated for 10 min, titania particles with an average particle size of 29 nm were obtained (Figure 2.6) This increase in particle size could be attributed to a possible dissolution-reprecipitation process occurring in the sol, on the larger particles at the expense of smaller particles.28
This is supported by the observations from the X-ray diffraction pattern of gel (Fig. 2.9) which gave well-defined anatase peaks.

![Figure 2.8. Differential thermal analysis curve of dried titania sol](image)

The DTA analysis shows (Figure 2.8) an endothermic peak below 150 °C is due to the removal of physically adsorbed water in the titania gel matrix. An exothermic peak in the region 270 °C is due to the evoluation of nitrate used for peptisation of the sol.

### 2.4.3 X-ray Diffraction analysis

The X-ray diffraction pattern of anatase phase of titania has a main peak at $\theta = 25.2^\circ$ corresponding to the 101 planes (JCPDS 21-1272) and the main peak of rutile phase is due to its 110 planes (JCPDS 21-1276) present at $\theta = 27.4^\circ$. X-ray diffraction patterns of the gel and the calcined powders are presented in Figure 2.9. A broad peak corresponding to the 101 plane peak of anatase phase is found in the X-ray diffraction pattern of 70 °C dried gel. This clearly indicates that the crystalline anatase is formed in the dried gel even at this low temperature. After calcination at 500 °C the crystalline
nature of titania increases, which resulted in distinct anatase peak in the X-ray diffraction pattern.

**Figure 2.9.** X-ray diffraction pattern of titania calcined at different temperatures (a) 70 (b) 500 (c) 600 (d) 700 (e) 800 (f) 850 °C. A stands for Anatase (101) plane and R is for Rutile (110) plane.

At 600 °C the anatase to rutile conversion starts and about 28% rutile was present in the system after calcination at 600 °C for 1h. While 71 % of titania is present in the rutile phase after calcination at 700 °C, the titania completely transformed to rutile phase at 800 °C. The anatase to rutile ratio and crystallite size calculated using Scherrer equation are given in Table 2.1. The crystallite size also increases with temperature and it is 12.8 nm at 500 °C and it further increased to 20 nm after 600 °C calcination. One of the important observations is that the phase transformation also occurs from anatase to rutile in this temperature range. On heating, anatase irreversibly transforms into rutile with a moderate exothermic contribution. As reported in the literature, anatase to rutile phase transformation occurs at a temperature between 500 and 800 °C.31
Table 2.1. Anatase to rutile percentages and crystallite size of titania calcined at various temperatures

<table>
<thead>
<tr>
<th>Calcination Temp. (°C)</th>
<th>Anatase: Rutile ratio</th>
<th>Crystallite Size of anatase (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>100:0</td>
<td>6</td>
</tr>
<tr>
<td>500</td>
<td>100:0</td>
<td>12.8</td>
</tr>
<tr>
<td>600</td>
<td>72:28</td>
<td>20</td>
</tr>
<tr>
<td>700</td>
<td>29:71</td>
<td>31.1</td>
</tr>
<tr>
<td>800</td>
<td>0:100</td>
<td>Rutile</td>
</tr>
</tbody>
</table>

However, it was recently demonstrated that a very low particle size (below 14 nm) causes the anatase phase to be thermodynamically stable.\(^{32}\) This may be the reason for the phase transformation occurring between 500 to 600 °C.

2.4.4 FTIR spectroscopy

The IR spectra of gels calcined at various temperatures presented in Figure 2.10a indicate a broad band between 3500 and 3000 cm\(^{-1}\), which is due to the presence of \(-\text{OH}\) groups on the surface of titania.\(^{33-35}\) The δ\(\text{H}_2\text{O}\) band around 1620 cm\(^{-1}\) demonstrates the presence of molecularly adsorbed water in the dried gel.\(^{35}\) The shift of the ν\(\text{OH}\) bands from 3750–3600 to around 3200 cm\(^{-1}\) is due to the presence of hydrogen bonding.\(^{36}\) On calcination at high temperature (Figure 2.10b & c), the peaks get sharpened with less intensity, indicating the removal of \(-\text{OH}\) groups from the surface. Calcination to high temperatures decreased the intensity of the 1624 cm\(^{-1}\) band (Fig. 2.10). The presence of small absorbance in the high temperature calcined samples around 1600 cm\(^{-1}\) may be due to the water adsorption on dehydroxylated anatase.\(^{37}\)
The sharp absorbance at 1348 cm$^{-1}$ in the gel (Fig. 2.10a) is due to the presence of nitrate species and is completely absent in the calcined samples. Ti–O–Ti bonds appear in the range 400–600 cm$^{-1}$ and the sharpness of the peak increases with increase of calcination temperature. No characteristic peaks corresponding to chemisorbed SO$_4^{2-}$ ions (1230, 1135, 1050 cm$^{-1}$) were observed in the prepared gel, indicating that the surface of anatase is SO$_4^{2-}$ free.

2.4.5 BET surface area analysis

Textural characteristics of the samples calcined at 500, 600, 700 and 800 °C derived from N$_2$ adsorption analysis is presented in Table 2.2. Specific surface area ($S_{BET}$), total pore volume calculated at $p/p_0 = 0.99$, BJH mesopore volume and micro pore
volume which were calculated by t-plot method and average pore diameter values are presented in Table 2.2.

**Table 2.2. N₂ adsorption characteristics of titania with calcination temperature**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micro pore volume (cm³/g)</th>
<th>Meso pore volume (cm³/g)</th>
<th>Average Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>48.7</td>
<td>0.1084</td>
<td>0.00392</td>
<td>0.1045</td>
<td>7.9</td>
</tr>
<tr>
<td>600</td>
<td>19.1</td>
<td>0.0478</td>
<td>0.00015</td>
<td>0.0477</td>
<td>10</td>
</tr>
<tr>
<td>700</td>
<td>6.51</td>
<td>0.0267</td>
<td>0.0005</td>
<td>0.0262</td>
<td>16.3</td>
</tr>
<tr>
<td>800</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Very low</td>
</tr>
</tbody>
</table>

On increasing the temperature, the surface area, total pore volume and mesopore volume also decrease. This may be due to an increase in crystallite size and densification or collapse in pore structure of titania. The adsorption isotherms (Figure 2.11) of the samples show type IV behaviour with typical hysteresis loop. This hysteresis loop is characteristic of mesoporous materials.₃⁹

**Figure 2.11.** Adsorption isotherm of titania calcined at (a) 500 (b) 600 °C
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The mesopore contributions towards the surface area of these samples are greater than that of the micropores. This is corroborated from mesopore volume and the micropore volume calculated by t-plot method. The micropore analysis indicated that the micropore volume decreases with increase of calcinations temperature, and is an evidence of the gradual collapse of the gel network when subjected to high temperature treatment. Titania powder calcined at 800 °C becomes almost nonporous as evidenced from the very low surface area which is less than 1 m²g⁻¹, and it is not possible to measure through our BET surface area analyser.

2.4.6 Transmission Electron Micrographs

The Transmission electron microscope images of titania sample calcined at 600 °C are presented in Figure 2.12. The bright field image indicate the mesoporous nature of the titania (Figure 2.12.A). The titania has a crystallite size of 23 nm.

Figure 2.12. TEM images of the titania sample calcined at 600 °C

The electron diffraction image (Figure 2.12.A1) indicates that the titania sample is crystallized and sharp diffraction pattern indicates the crystallinity.
2.5 Conclusion

An aqueous sol-gel method for the preparation of titania sol using titanyl sulphate precursor was successfully developed. The stability of the sol was monitored using zeta potential measurement. The sol is stabilized both in acidic (below pH 2.5) and basic (above pH 7.5) region and the smallest particle size was obtained in the acidic range. An average particle size of 27 nm was obtained for the sol peptised at pH 2. The sol was aged for about 6 months and it was found that the sol was very stable. The X-ray diffraction image indicates that the anatase to rutile phase transformation starts above 500 °C and completes at 800 °C. The Transmission electron micrograph image indicates that the average crystallite size of titania prepared through aqueous sol-gel method is 23 nm at 600 °C.

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