Chapter 4: Development of Functional Coatings on Porous Alumina and Glass Substrate

4.1 Development of Ultra Filtration Membrane on Porous Alumina Substrate

4.1.1 Abstract

Ceramic membranes are of interest because of their higher chemical, thermal and mechanical stability than all other membrane materials. These membranes allow filtration under extreme conditions, like high temperature and extreme pH. In this chapter the fabrication of alumina-titania multilayer ceramic membrane layers on porous alumina support is described. The coating precursor is made from boehmite and titania sols, which is prepared through aqueous sol-gel route. Different compositions of coating solutions are prepared using boehmite and titania sols with hydroxyethyl cellulose (HEC) as binder. The various coating compositions prepared were characterised by viscosity measurements, TGA and DTA. Unsupported membranes were first prepared to check crack free drying and to study the porosity features of the membranes. The compositions corresponding to crack-free and thin membranes were chosen for coating on porous alumina substrates. Thus the one containing 1.5% HEC and 0.4% boehmite was coated as an intermediate layer. The top layer was formed with the composition containing 1% HEC and 0.2% titania. The membranes were characterised by XRD, FTIR and surface area measurements. The morphological features of coated layer were studied using scanning electron microscope. The filtration property of the membrane has been examined by cross-flow filtration method using a colouring agent such as congo red which is a red coloured dye. About 99.3% rejection of congo red was observed.
4.1.2 Introduction

Ceramic membranes are a class of engineering ceramic systems having great potential for application in the field of water desalination, ultrafiltration and separation of gas mixtures. They are also projected as potential candidates for catalytically active and carrier membranes. Ceramic membranes are thin (few nanometers to few micrometres thick) planar structures formed, either as supported or as unsupported configuration by the regular packing of fine ceramic particles (2 to 1 nm) or inorganic polymer clusters. The first ever application of ceramic membranes dates back to the 1940’s, after the second World war. They were used for the enrichment of U$^{235}$. In that process, U$^{235}F_6$ was separated from a mixture of U$^{238}F_6$ and U$^{235}F_6$ using a supported membrane in a tubular configuration. Commonly used materials for making ceramic membranes are Al$_2$O$_3$, TiO$_2$, SiO$_2$, ZrO$_2$ or a combinations of these materials. Aluminium, titanium and zirconium are considered as the three most common porous membrane materials. There are also reports on oxide membranes with minor amounts of dopants to improve the thermal and chemical stability. Doping and surface modification can also improve the catalytic performance of the membranes. There are many reports for the preparation of membranes employing solid state-particle-sintering, sol-gel, anodic oxidation, chemical vapour deposition phase separation and leaching and the reverse micelle method. Out of these methods, solid state-particle-sintering and sol-gel process are considered to be the practical methods. Usually ceramic microfiltration membranes are prepared by solid state-particle-sintering method in which the membranes are fabricated with particles by coating the support and then sintering to form a membrane skin which is chemically attached to the support. Pore size obtained by this
method varies from 0.1 to 1 \mu m and the porosity of the ceramic membranes is in the range of 30-50%. Ceramic ultra filtration membranes are generally prepared by the sol-gel methods. By sol-gel method, the mean membrane pore size mainly assembles between 2 and 20 nm. The sol-gel process involves the hydrolysis and condensation of various metal alkoxide molecules under controlled conditions to form metal-oxygen-metal bridging units. Microporous alumina membranes are used for separation of microbes from drinking water, concentration of fruit juices in food industry and filtration of beverages for their clarification and sterilization. They also find application as substrate for nanofiltration, ultrafiltration and reverse osmosis membranes.

4.1.2.1 Structural features of supported ceramic membranes

Supported ceramic membranes consist of a macroporous support which is a few millimeters thick (Figure 4.1.1) with an average pore diameter of 1 to 15 \mu m and with a porous intermediate layer of 10 to 100 \mu m thick. The average pore diameter of the porous intermediate layer is 100-1500 nm. The third top layer, which is the functional membrane layer, usually has a thickness of 0.1 to 10 \mu m with an average pore diameter in the range of 1-100 nm (Table 4.1.1).
Figure 4.1.1 (A) SEM photo and (B) a schematic representation of an asymmetric composite membrane (C) Cross sectional view of porous membrane support tube

Table 4.1.1 Properties of membrane layers

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
<th>Average pore diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al₂O₃-support</td>
<td></td>
<td>1.4µm</td>
</tr>
<tr>
<td>α-Al₂O₃-MF</td>
<td>20-25 µm</td>
<td>0.18µm</td>
</tr>
<tr>
<td>Coarse ZrO₂-UF</td>
<td>10 µm</td>
<td>60 nm</td>
</tr>
<tr>
<td>Coarse TiO₂-UF</td>
<td>10 µm</td>
<td>50 nm</td>
</tr>
<tr>
<td>Fine ZrO₂-UF</td>
<td>100-200 nm</td>
<td>2-3 nm</td>
</tr>
<tr>
<td>Fine TiO₂-UF</td>
<td>500 nm</td>
<td>10 nm</td>
</tr>
<tr>
<td>ZrO₂-NF</td>
<td>&lt;50 nm</td>
<td>1-2 nm</td>
</tr>
<tr>
<td>TiO₂-NF</td>
<td>&lt;50 nm</td>
<td>1-2 nm</td>
</tr>
</tbody>
</table>
4.1.2.2 Formation steps of ceramic membranes

The important step in the preparation of sol-gel derived ceramic membranes is the preparation of a stable colloidal sol. The size and nature of the agglomerates in the sol is very important because they affect the ease of formation and the final nano structure of the membranes. The exact role of the agglomerates is that they influence the top-layer growth kinetics. In fact, the agglomerates must be weak and below a certain size in order to give small pores and a narrow pore size distribution.\textsuperscript{25} In general, a colloidal sol yields a membrane with pore size in the mesopore range while inorganic polymer solutions yield microporous membranes.

The next step is to apply the sol / solution (dip solution) on a porous support by bringing one side of the support (in the case of flat plate supports) in contact with the dip-solution. An alcogel or a hydrogel layer will be formed on the support and the layer formation mechanism can be film coating or a combination of slip-casting and film coating.\textsuperscript{26} The film coating process depends on the viscosity of the dip-solution and the pulling speed of the support from the dip-solution. On the other hand, the slip-casting process depends on the pore characteristics of the support as well as on the viscosity and the surface tension of the dip-solution. After forming an alcogel or a hydrogel layer, the membrane-support system is dried at controlled temperature and relative humidity. The dipping stage is absent in the preparation of unsupported membranes. They are formed simply by pouring the dip-solution into a glass or a polyethylene petri dish and dried directly to get the xerogel. Drying is one of the most important steps in the preparation of ceramic membranes. During drying, large stresses develop due to the
capillary tension of the pore fluid and these stresses are not relaxed by shrinkage because of the presence of rigid support.

Figure 4.1.2. Flow chart illustrating the formation of ceramic membranes using sol-gel process.

The stress field in the top-layer can become inhomogeneous around hard agglomerates.

This makes the membrane top-layer to crack and peel off from the support. Drying
stresses also have a positive role in membrane formation. The stresses cause weak aggregates to break down and may help in further rearrangement and ordering of the primary particles.27 The final nano structure of the membrane is believed to be established at this stage. There exists a maximum and minimum allowable thickness which should not be surpassed if defect (crack) free membranes have to be obtained. The actual thickness limit depends on the membrane material.28 The last step is calcination, which gives the mechanical integrity to the membrane-support system. During calcination, physically adsorbed water, hydroxyls, residual organics and nitrates will escape below 450 °C. Flow chart for the preparation of membrane using sol-gel method is presented in Figure 4.1.2.

4.1.2.3 Filtration technology

Filtration technology using membranes has a wide range of applications. So far, organic filters commonly have been used, although these filters have relatively low temperature limitations (typically <200°C) and lack chemical stability. As a new kind of membrane, ceramic filters have a potential capability for replacing organic filters for some applications; because of their superior high temperature (>1000°C) and chemical stability. Ceramic filters are expected to be used in applications such as microfiltration (100 nm < pore size < 10 μm), ultrafiltration (pore size<100 nm), filtration of molten metal, gas separation at high temperature and particle removal from exhaust gas from diesel engines (Figure 4.1.3).29 Filtration performance of various type of membranes are given in Table 4.1.2.
Figure 4.1.3. Diagramatic representation of classification of various types of membranes

Table 4.1.2. Filtration performance of various types of membranes

<table>
<thead>
<tr>
<th>Components retained by membrane</th>
<th>Microfiltration</th>
<th>Virus Filtration</th>
<th>High-Performance Filtration</th>
<th>Ultrafiltration</th>
<th>Nanofiltration/Reverse osmosis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intact cells Cell debris</td>
<td>Proteins</td>
<td>Proteins</td>
<td>Proteins</td>
<td>Antibiotics Sugars Salts</td>
<td></td>
</tr>
<tr>
<td>Components passed through membrane</td>
<td>Colloidal material Viruses Proteins Salts</td>
<td>Proteins Salts</td>
<td>Proteins Salts</td>
<td>Small peptides Salts</td>
<td></td>
</tr>
<tr>
<td>Approximate membrane cutoff range</td>
<td>0.05µm-1µm</td>
<td>100kD-0.05µm</td>
<td>10kD-300kD</td>
<td>1kD-1000kD</td>
<td>&lt;1kD</td>
</tr>
</tbody>
</table>

For membranes used for liquid phase separation, the driving force is mechanical pressure difference, and they are categorized into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), depending on their pore sizes (Figure
4.1.3). Microfiltration membranes have pore sizes between 100 and 1000 nm and UF and NF are classified at the pore size less than 100 nm. RO membranes have smaller pore size than 1 nm. According to conventional definition and for the convenience of membrane users, molecular weight cut-offs (MWCO) which are based on permeation performance are also often used. NF membranes are categorized to have MWCO between 200 and 1000.\textsuperscript{30, 31} Filtration performance of various types of membranes were given in Table 4.1.2.

4.1.2.4 Applications of ceramic membranes

Initially ceramic membranes were used in waste water technology. Meanwhile, successful solutions and possible applications cover all industries.

- Chemical industry
  (a) Product separation and cleaning (b) Concentration of polymer suspensions and metal hydroxide solutions (c) Separation of catalysts (d) Recovery of dyes and pigments (e) Desalination of products (f) Cleaning and recycling of organic solvents (g) Metal industry / Surface engineering (h) Recycling and disposal of degreasing and rinsing baths (i) Treatment of oil / water emulsions (j) Recovery of heavy metals (k) Cleaning of waste water from grinding processes (l) Treatment of waste water from glass and glass fibre production

- Biotechnology
  (a) Concentration, fractionation, isolation and sterilization of antibiotics, enzymes, proteins, amino acids and vitamins (b) Separation, concentration and dewatering of biomass and algae (c) Disposal of fat emulsions (d) Separation of yeast
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- Food and beverages

(a) Clarification of juice and beer (b) Concentration of juice (c) Sterilization of milk and whey (d) Separation and fractionation of milk and whey ingredients (e) Desalination of whey (f) Dewatering of products (g) Purification of drinking water

- Recycling and environment

(a) COD / BOD reduction (b) Oil / water separation (c) Recovery of pharmaceuticals and pesticides (d) Retention of microorganism (e) Retention of heavy metals and radioactive substances (f) Recycling of water from swimming pools (g) Purification of the drain of sewage plants.

4.1.2.5 Benefits of ceramic membranes

(a) Long and reliable lifetime (b) High resistance to temperature and pressure (c) High stability to organic media (d) Rigidity with no creep or deformation (e) Stability over a wide pH range (f) Corrosion and abrasion resistance (g) Insensitivity to bacterial action (h) Can be repeatedly sterilized by steam or chemicals (i) Ability to be backwashed (j) Consistent pore size (k) Can process highly viscous fluid (l) Possibility of regeneration after fouling (m) Membranes are bonded to substrate by strong ceramic bonds.

4.1.2.6 Disadvantages of ceramic membranes

(a) Brittle and poor geometrical stability (b) Needs to be in the supported configuration (c) High installation and maintenance costs (d) Sealing is very difficult for high temperature application.

Ceramic membranes have a wide variety of applications in chemical industries, food and beverage industries, biotechnology, water purification and recycling etc. The
general mode of adapting ceramic membranes to the different application domains, in particular for liquid filtration, has been to superpose successive porous layers starting from a macroporous support. In order to minimize flow resistance, non interpenetrated layers are superposed with decreasing pore sizes and thicknesses. The resulting multilayered ceramic structures must be regarded as advanced ceramic materials with unique fluid processing performance. Research is actively done in this area of development of membrane with desired pore structures. Normally all the sol-gel membrane formation starts with alkoxide precursors. To the best of our knowledge there is no report on the preparation of multilayered membrane through an aqueous sol-gel method. The objective of the present work is the development of an aqueous sol-gel method for the preparation of mesoporous membrane layer on the surface of porous alumina substrate for ultra filtration applications.

4.1.3 Experimental

Al(NO$_3$)$_3$.9H$_2$O, ( sd. Fine Chemicals, India Ltd ) 125 g was dissolved in 1 litre water. The solution was heated to 90 °C. Keeping the temperature constant at 90 °C, ammonium hydroxide solution was added drop wise. Addition was continued till the precipitation was complete at pH 8. The precipitate was filtered while solution was hot and washed with distilled water till it becomes free from nitrates. The precipitate was aged for 24h. It was peptised to a stable sol by the addition of 10% HNO$_3$ at a pH of 3.5. The particle size of the sol was measured using Malvern Zetasizer 3000 HS (U.K) particle size analyzer. Alumina coating solutions of different compositions were prepared using boehmite sol with hydroxyethyl cellulose (HEC) as the binder. The calculated amount of hydroxyethyl cellulose was dissolved in water and added into the boehmite
sol. The resultant solution was homogenized by stirring for half an hour by gentle warming followed by centrifugation. The different wt% of boehmite and hydroxy ethyl cellulose are provided in Table 4.1.3. The viscosities of the above compositions were measured to study the variation of viscosity with shear rate using a Viscorheometer (Rheo Labmc1, Physica, Anton Paar, Germany)

Table 4.1.3. Alumina coating solutions of different compositions were prepared using boehmite sol with hydroxyl ethyl cellulose

<table>
<thead>
<tr>
<th>Percentage composition of HEC</th>
<th>Percentage composition of Boehmite</th>
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<tbody>
<tr>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>1.5</td>
<td>0.1</td>
</tr>
<tr>
<td>1.5</td>
<td>0.2</td>
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<tr>
<td>1.5</td>
<td>0.3</td>
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<tr>
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<td>0.4</td>
</tr>
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<td>0.5</td>
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<tr>
<td>2</td>
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<td>2</td>
<td>0.3</td>
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<tr>
<td>2</td>
<td>0.4</td>
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<tr>
<td>2</td>
<td>0.5</td>
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<tr>
<td>2.5</td>
<td>0.1</td>
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<td>2.5</td>
<td>0.2</td>
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<tr>
<td>2.5</td>
<td>0.3</td>
</tr>
<tr>
<td>2.5</td>
<td>0.4</td>
</tr>
<tr>
<td>2.5</td>
<td>0.5</td>
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</tbody>
</table>
Titanyl oxysulphate (TiOSO₄, Aldrich Chemicals, 99.99% purity) was used as precursor for the synthesis of titania sol. In a typical experiment, titanyl oxysulphate was dissolved in 500 ml of distilled water (0.2 M) and hydrolysed by slow addition of ammonium hydroxide (10%, sd. Fine Chemicals, India Ltd) solution under constant stirring at room temperature (32 °C), until the reaction mixture attained pH 8.5. The precipitate obtained was separated by filtration and was washed free of sulphate ions (confirmed by the BaCl₂ test) with distilled water. The precipitate was further dispersed in 1000 ml of hot distilled water and peptised by addition of 10% HNO₃ (Merck, India Ltd) solution. A stable sol was obtained at a pH range of 1.7 to 2.2. Different compositions of coating solutions were prepared by mixing titania sol with hydroxyethyl cellulose dissolved in water (HEC). The compositions were stirred for half an hour and then centrifuged. The compositions prepared were given in Table 4.1.4.

Various compositions of coating solutions prepared from boehmite and titania sols were used for making unsupported membranes. Particle size distribution of the sol was analyzed by Malvern Zetasizer 3000 HS particle size analyzer. 20 ml of the different compositions were poured into separate clean plastic petri dishes and were dried in a humidity chamber at 50 °C and at 60% relative humidity for 24h followed by drying at 70 °C. The composition which gave crack free membrane of desired viscosity was chosen for coating purpose. The porous alumina tubes were cleaned well by boiling several times in distilled water and were subsequently dried. Then the tube to be coated was held in the vertical direction with the help of a support stand. A glass tube was attached to the upper end of the porous alumina tube. The lower end of alumina tube was connected to a glass column. The column was lowered beyond the position of the tube and the coating
solution prepared from boehmite sol and hydroxyethyl cellulose of suitable composition and which showed crack-free behaviour when tested as unsupported membrane was introduced into the column.

Table 4.1.4. Titania coating solutions of different compositions prepared using boehmite sol with hydroxylethyl cellulose

<table>
<thead>
<tr>
<th>Percentage composition of HEC</th>
<th>Percentage composition of Titania</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>1.5</td>
<td>0.1</td>
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<tr>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>1.5</td>
<td>0.4</td>
</tr>
<tr>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The column containing the coating solution was slowly raised so that the solution rises through the porous alumina tube until it reaches the glass tube attached to the upper portion of the alumina tube. The column was then lowered slowly at a speed of 20 cm per min. so that the level of coating solution also slowly lowered. The coated tubes were dried in a humidity chamber at 50 °C and 60% relative humidity for 24h and then dried at 70 °C. The dried coated tubes were calcined at 800 °C for 5h at a heating rate of 1 °C per
minute followed by atmospheric cooling. Thus an intermediate layer was formed in the alumina tubes.

The top layer was coated in the tubes with the coating solution made from titania sol and hydroxyethyl cellulose. The coating procedure was exactly the same as for coating of intermediate layer. A schematic diagram of coating unit is given in Figure 4.1.4.

![Schematic diagram of the coating process for the membrane on the inner surface of the tubular support](image)

**Figure 4.1.4.** Schematic diagram of the coating process for the membrane on the inner surface of the tubular support (1) coating solution tank; (2) soft tube; (3) valve; (4) tubular membrane; (5) glass tube

The coated tubes were dried in a humidity chamber at 50 °C and 60% relative humidity for 24h followed by drying at 70 °C. The dried coated tubes were calcined at 500 °C for 3h at a heating rate of 1 °C per min. followed by atmospheric cooling. The TGA and DTA analysis was carried out in the dried coating solutions at a heating rate of 10 °C min$^{-1}$ using a Thermogravimetric analyzer (Shimadzu, TGA 50H, Japan) and Differential thermal analyzer (Shimadzu, DTA 50H, Japan). The surface area measurements and pore analysis were carried out by nitrogen adsorption using Micromeritics Gemini 2375.
surface area analyser after degassing each sample at 200 °C for 2 h. XRD patterns of the calcined gels were taken in a Philips X'pert X-ray diffractometer in the diffraction angle 2θ range 10-80° using Cu Kα radiation. The morphology of membrane layer was observed by a Scanning Electron Microscope (SEM JEOL JSM-6700F). Ultrafiltration studies were carried out with Congo red (Mw 696.66 g/mol), a red coloured dye, using indigenously developed flux measurement set up and the photograph of the unit is presented in Figure 4.1.5. The equipment consists of support-holding chamber, a dosing pump, water reservoir, inlet and outlet flow meter, pressure gauge and an open end for collecting the filtrate. Two alumina porous tube supports of dimensions 17 cm length and 8.5 mm diameter can be fixed in the support chamber. The schematic arrangement of the flow stream is presented in Figure 4.1.6.

Figure 4.1.5. Photograph of the filtration set up
Chapter IV

Controller (Pressure and Flow)

Figure 4.1.6. Schematic representation of filtration setup

The feed is pumped by a positive displacement pump (reciprocating) from a sump through the inlet to the substrate and the retenate was allowed to go back to the sump in a closed loop manner. A controller is provided at inlet line to control the line pressure and flow rate. The filtrate is collected down in a measuring cylinder over definite time interval. The flux is calculated at different time intervals and a plot was made against time vs. flux. By knowing the concentrations of the feed and the filtrate, the percentage of rejection by the membrane is calculated.
4.1.4 Results and discussions

4.1.4.1 Particle size measurements

Figure 4.1.7 (a) and (b) shows the particle size distribution of boehmite and titania sol prepared through an aqueous sol-gel method. Boehmite sol shows unimodal particle size distribution having an average size of 165 nm and titania sol also shows unimodal particle size distribution having an average size of 27 nm. This sol is further used for the preparation of alumina and titania membrane.

![Particle size distribution curves](image)

**Figure 4.1.7.** Particle size distribution curves of (a) boehmite sol and (b) titania sol.

4.1.4.2 Viscosity measurements

The viscosity curves of the different coating compositions prepared using boehmite sol and hydroxyethyl cellulose (HEC) are shown in Figure 4.1.8 a, b, c & d. It is seen that viscosities of all compositions vary with different shear rate. There is a sudden increase in viscosity upto a particular shear rate and after that it shows a gradual decrease. The increase in viscosity corresponds to the gelation of sol particles with...
hydroxyethyl cellulose. The decrease in viscosity is due to the collapse of gel structure with a further increase in shear rate.

**Figure 4.1.8.** a, b, c & d. Viscosity curves of various coating compositions prepared with boehmite sol and hydroxyethyl cellulose (HEC).

The viscosity curves of titania and hydroxy ethyl cellulose are given in Figure 4.1.9a, b & c. The viscosities of all compositions except 1% HEC + 0.1% Titania, 1% HEC + 0.5% Titania and 1.5% HEC + 0.1% Titania are initially high due to the fact that the suspension
structure is close to equilibrium. Hence the movement of the particles dominates over the viscous force (first Newtonian region).  

Figure 4.1.9. a, b & c. Viscosity curves of various coating compositions prepared with titania sol and hydroxyethyl cellulose (HEC)

At high shear rates, the viscous forces affect the suspension structure and shear thinning occurs due to progressive breakdown of particulate network or agglomerates (floc). At very high shear rates, viscous forces dominate and normally a plateau in viscosity is observed (second Newtonian region) indicating completely hydrodynamically (arising from the shear field) controlled structure. The remaining three compositions show a small increase in viscosity up to a particular shear rate due to gel formation with
hydroxyethyl cellulose (HEC) and a small decrease in viscosity is observed due to collapse of gel structure with further application of shear rate.

### 4.1.4.3 Analysis of unsupported membrane

The photographs of the unsupported membranes prepared using different coating compositions of alumina (boehmite) sol and hydroxyethyl cellulose (HEC) are shown in Figure 4.1.10.

![Figure 4.1.10.](image)

**Figure 4.1.10.** (I) 1% HEC (II) 1.5% HEC (III) 2% HEC (IV) 2.5% HEC (a) 0.1% Boehmite, b) 0.2% Boehmite, c) 0.3% Boehmite, d) 0.4% Boehmite, e) 0.5% Boehmite.
The cracking behaviour of the unsupported alumina membranes was studied. The unsupported membrane contains 1% HEC + 0.4% boehmite, 1.5% HEC+ 0.3% boehmite and 1%HEC+ 0.5% boehmite cracked during drying. Upon considering the viscosity of the coating composition, thickness and crack free formation of unsupported membrane, we adopted a composition 1.5% HEC + 0.4% boehmite which could easily give a crack free alumina membrane intermediate layer on porous ceramic substrate.

The photographs of unsupported membranes prepared with different coating compositions of titania sol and hydroxyethyl cellulose (HEC) are shown below in Figure 4.1.11. The cracking behaviour of the unsupported titania membranes was studied. The unsupported membrane containing 1% HEC + 0.3% titania, 1% HEC + 0.4% titania, 1% HEC + 0.5% titania and 1.5% HEC + 0.5% titania cracked during drying.

Figure 4.1.11. (I) 1% HEC (II)1.5% HEC (III) 2% HEC a) 0.1% Titania, b) 0.2% Titania, c) 0.3% Titania, d) 0.4% Titania, e) 0.5% Titania.
Upon considering the viscosity of the coating composition, thickness and crack free formation of unsupported titania membrane, we adopted a composition (1% HEC + 0.2% titania) which could easily give a crack free titania membrane top layer on porous ceramic substrate.

4.1.4.4 Thermo gravimetric and Differential thermal analysis

Figure 4.1.12 a & b shows the Thermo Gravimetric and Differential Thermal analysis profiles of the unsupported alumina membrane (1.5% HEC + 0.4% Boehmite) dried at 50 °C and at 60% relative humidity for 24h.

![Figure 4.1.12. TGA and DTA curves of 1.5% HEC- 0.4% Boehmite composition.](image)

In the TGA curve (4.1.12a), the percentage of weight loss is 21.87% up to 190 °C due to the elimination of physically adsorbed water. A weight loss of 5.59% is observed in between 191 to 240 °C, which is attributed to due to the loss of nitrate. Similarly a weight loss of 51.57% is observed in between 241 to 540 °C resulting from the decomposition of hydroxyethyl cellulose (HEC) and removal of structurally adsorbed water. Beyond 540 °C, there is no obvious weight loss in the TGA curve.
In the DTA curve (4.1.12b) an endothermic peak at 106 °C corresponds to the elimination of physically adsorbed water. The exothermic peak at 205 °C is due to the loss of nitrate. The exothermic peak at 370 °C corresponds to the decomposition of hydroxyethyl cellulose (HEC).

Figure 4.1.13 shows the TGA and DTA curves of the unsupported titania membrane (1% HEC + 0.2% Titania) dried at 50 °C and at 60% relative humidity for 24 h.

Figure 4.1.13. TGA and DTA curves of 1% HEC-0.2% Titania composition.

In the TGA curve (4.1.13 a), percentage of weight loss is 17% up to 185 °C, which is the results of elimination of physically adsorbed water. The percentage weight loss between 186 to 220 °C is 1.22% which is due to the loss of nitrate. The percentage weight loss from 221 °C to 500 °C is 43% due to consequence of decomposition of hydroxyethyl cellulose (HEC) and removal of chemically coordinated water. There is no major weight loss observed after 500 °C. In the DTA curve (4.1.13b), endothermic peak centered around 100 °C is the result of removal of physically adsorbed water. The
exothermic peak at 190 °C corresponds to the loss of nitrate. The exothermic peak at 320 °C results from the decomposition of hydroxyethyl cellulose (HEC).

4.1.4.5 X-ray diffraction analysis

Powder X-ray diffraction pattern of unsupported alumina membrane (1.5% HEC + 0.4% Boehmite) calcined at 800 °C for 5 h is shown in Figure 4.1.14(a). The peaks correspond to the γ- alumina formed on calcination. The XRD pattern is not sharp due to the spinel structure of γ- alumina formed. The XRD pattern of unsupported titania membrane (1% HEC + 0.2% Titania) calcined at 500 °C for 3h is shown in Figure 4.1.14 (b). The broad peak at 2θ value 25.3° is the characteristic (101) plane peak of nanocrystalline anatase titania. From these observations, we can conclude that a γ- alumina intermediate layer and a nanocrystalline
titania top layer were formed in the porous alumina support during the fabrication of membrane layer.

4.1.4.6 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of unsupported alumina membrane (1.5% HEC + 0.4% Boehmite) calcined at 800 °C for 5h (Figure 4.1.15.a) and unsupported titania membrane (1% HEC + 0.2% Titania) calcined at 500 °C for 3h (Figure 4.1.15b) is shown in Figure 4.1.15.

![FTIR Spectrum](image)

**Figure 4.1.15.** FTIR Spectrum of (a) unsupported alumina membrane calcined at 800 °C for 5 h and (b) unsupported titania membrane calcined at 500 °C for 3 h.

In the FTIR spectrum of unsupported alumina membrane calcined at 800 °C (Figure 4.1.15 a) the band at 3443 cm$^{-1}$ corresponds to the stretching vibration of O-H bond that results from co-ordinated water on the alumina surface. The bands at 1646 cm$^{-1}$ is due to the bending vibration of O-H bond, which is related to absorbed water. The strong broad band between 500 and 750 cm$^{-1}$ and centered at 579 cm$^{-1}$ is due to the vibrations of AlO$_6$ (ν AlO$_6$). The strong broad band between 900 and 750 cm$^{-1}$ and centered at 791 cm$^{-1}$ is
Chapter IV

assigned to the vAlO₄ vibrations. From this observation, it is concluded that both octahedral and tetrahedral alumina species are present in the system.

The FTIR spectrum of titania 4.1.15 (b) shows bands at 3450 cm⁻¹ and 1626 cm⁻¹ which corresponds to the stretching and bending vibrations of hydroxyl group. The band below 1000 cm⁻¹ is due to the stretching vibrations of Ti-O-Ti network.

4.1.4.7 BET Surface area analysis

The adsorption isotherm and pore size distribution curve of unsupported alumina membrane calcined at 800 °C for 5h are shown in Figure 4.1.16 (a) and (b) respectively. The adsorption isotherm is of type IV which is characteristic of mesoporous material. The pore size distribution curve is bimodal, one is below 6 nm (60 angstrom) and other one is below 40 nm (400 angstrom). An average pore diameter of 10.5 nm is obtained.

![Figure 4.1.16](image)

**Figure 4.1.16.** (a) Adsorption isotherm and (b) Pore size distribution curve (inset) of unsupported alumina membrane calcined at 800 °C for 5 h.
The adsorption isotherm and pore size distribution curve of unsupported titania membrane calcined at 500 °C for 3h are shown in Figure 4.1.17 (a) and (b) respectively. The adsorption isotherm is of type IV which is characteristic of mesoporous material. The pore size distribution curve is bimodal, one is below 4 nm (40 angstrom) and other one is below 30 nm (300 angstrom). An average pore diameter of 13 nm is obtained.

![Figure 4.1.17. (a) Adsorption isotherm and (b) Pore size distribution curve (inset) of unsupported titania membrane calcined at 500 °C for 3 h.](image)

**Table 4.1.5.** Surface area results of unsupported alumina membrane calcined at 800 °C for 5 h & unsupported titania membrane calcined at 500 °C for 3 h.

<table>
<thead>
<tr>
<th></th>
<th>BET Surface Area (m²g⁻¹)</th>
<th>Total Pore Volume (cm³g⁻¹)</th>
<th>Average Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsupported alumina membrane calcined at 800 °C for 5h</td>
<td>108.3</td>
<td>0.2848</td>
<td>10.5</td>
</tr>
<tr>
<td>Unsupported titania membrane calcined at 500 °C for 3h</td>
<td>76.7</td>
<td>0.2498</td>
<td>13.0</td>
</tr>
</tbody>
</table>
The surface area results are given in Table 4.1.5. From these observations it is concluded that a mesoporous alumina and titania multi layer membrane are successfully formed on the porous alumina support.

4.1.4.8 Scanning Electron Microscopy (SEM)

The morphological features of uncoated and coated substrates can be studied by Scanning Electron Microscopy (SEM). The SEM pictures of uncoated and alumina coated alumina substrates are shown in Figures 4.1.18 (a) and (b). The fracture of the alumina coated substrate is provided in Figure 4.1.18(c).

![SEM images](image)

**Figure 4.1.18.** SEM images of (a) porous alumina surface (uncoated) (b) alumina coated surface (c) fracture of the coated porous alumina substrate.

The integrity of the membrane layer and its incorporation with the porous Al₂O₃ substrate are crucial factors in the fabrication of defect-free membrane since even few cracks, pin-
holes or breakage of weak joints can cause failure of the separation efficiency. Examining the SEM images (plain view) of membrane layer shown in Fig. 4.1.18b we observe that this method is successful to fabricate membrane layer with good integrity and without significant cracks or pin-holes.

From the SEM images, it is observed that a uniform coating layer was formed on the surface of porous alumina substrate. From the fracture micrograph a coating layer of thickness approximately ~1-2 μm is formed on porous alumina substrate. The second layer of titania composition having a particle size of 27 nm was formed over the alumina layer and the total thickness of the layer became ~4-5 μm. This was further used for the ultra filtration application. The scanning electron micrographs of the alumina-titania multilayer coating is given in Figure 4.1.19 a, b & c

![SEM images of fracture of the Alumina–titania multi layer coated porous alumina substrate.](image)

**Figure 4.1.19.** SEM images of (a) (b) & (c) fracture of the Alumina–titania multi layer coated porous alumina substrate.
4.1.4.9 Filtration studies

The multi-layered membrane fabricated with alumina as intermediate layer and titania as top layer was used for cross-flow filtration studies. Congo red (696.66 g/mol), a red coloured dye, was dissolved in water (200 mg/l) and used as the colouring agent in the feed. The molecular structure of the Congo red dye is given in Figure 4.1.20. The filtration was performed for 10h and the flux was measured at 15 minute intervals. An average flux rate of 40 l/m².h.b is obtained. The permeation flux versus time curve is given in Figure 4.1.21. This flux rate is comparable to the flux rate observed in other ultra filtration membranes.37

![Molecular structure of Congo red](image)

Figure 4.1.20. Molecular structure of Congo red

The filtrate collected after 10h of filtration was analyzed by UV-Visible spectroscopy for determining rejection rate of membrane in the case of Congo red. A standard plot showing concentration Vs. absorbance of the standard samples is shown in Figure 4.1.22. The absorbance of the filtrate was compared with the standard curve. An absorbance value of 0.061 was observed and from the standard plot, concentration of Congo red in the filtrate was found to be 1.2743 mg/l.
Figure 4.1.21. Permeation flux of alumina-titania multilayer membrane during cross flow filtration with Congo red.

Figure 4.1.22. Standard curve of Concentration (mg/l) vs. Absorbance of congo red dye.

The membrane prepared through the present method showed a very high rejection (~99%) of 'Congo Red' (mol. wt. 696.66 g/mol). From these measurements a cut-off value of around 1000 Da can be deduced.37
4.1.5 Conclusions

Successful fabrication of alumina-titania multi-layer ceramic membrane on porous alumina substrates was achieved. The coating compositions prepared from boehmite and titania sols with hydroxyethyl cellulose (HEC) as binder were characterised by viscosity measurements, TGA and DTA. Unsupported membranes were prepared and their cracking behaviour was studied. The composition which corresponds to crack-free thin layers was chosen for coating on substrates. The membranes were characterised by XRD, FTIR and Surface area measurements. The morphological features of the membranes were studied using Scanning Electron Microscopy. The filtration property of the membrane was examined by filtration test using congo red as a colouring agent. About 99.3% rejection was observed with congo red. A membrane layer having a molecular cut off value around 1000 Da was developed.
4.2 Development of Photoactive Titania Coating on Glass Surfaces

4.2.1 Abstract

A uniform nanolayer of alumina doped titania coating has been developed on glass surface through an aqueous sol-gel method starting from titanylsulphate and aluminium nitrate as precursor. The thermo gravimetric analysis has been used to study the decomposition characteristic of coating precursor. The UV-Visible absorption spectrum shows that the absorption edge is blue shifted in the presence of alumina in the titania matrix. Scanning Electron Micrographs show that a uniform thin layer was formed on the glass surface. The Type IV behaviour shown by the pure and alumina doped titania powder indicates the mesoporous nature of the titania thin film formed on the glass surface. The 10 mol% alumina doped titania coating powder shows two times higher surface area than pure titania powder. Anatase phase was detected in both pure and 10 mol% alumina coated samples by Raman spectra. The alumina doping increases the photoactivity of titania film and the maximum photoactivity is observed for 2 mol% alumina doped titania film.

4.2.2 Introduction

Titania films have attracted attention due to their applications in anti-bacterial, self-sterilizing, self-cleaning, antisoiling and antifogging coatings. Of the different polymorphic forms of titania, anatase was found to be more photo catalytic active and useful in such type of coatings. For the fabrication of these titania thin layer, sol-gel method was found to be a promising one. The deposition of TiO₂ film by sol-gel method has been reported by few authors. Almost all sol-gel process start from alkoxide precursor. But for the bulk production of these coating an alkoxide process is
not found to be economically viable. Kishimoto et al. demonstrated the wettability of titania coating films by sol-gel method using an aqueous solution of Ti(SO)₄ containing polyvinyl pyrrolidone (PVP) as the coating solution. Ichinose et al. demonstrated the preparation of peroxo titanic acid (PTA) sol derived from TiCl₄ for the preparation of titania film. Lee et al. prepared and characterised peroxo titania sol from TiCl₃. Ge et al. prepared the autoclaved sol for the preparation of titania film using titanyl sulphate and H₂O₂. To best of our knowledge no work has been reported for the preparation of alumina doped titania film using simple aqueous sol-gel method. So in the present study an aqueous sol-gel method was developed for the preparation of titania film doped with alumina. Further it was characterized using scanning electron microscopy, atomic force microscopy and photoactivity studies.

4.2.3 Experimental

Titanyl oxysulphate (TiOSO₄, Aldrich Chemicals, 99.99% purity) was used as precursor for the synthesis of titania sol. In a typical experiment, titanyl oxysulphate was dissolved in 500 ml of distilled water (0.2 M) and hydrolysed by slow addition of ammonium hydroxide (10%, sd Fine chemicals, India Ltd) solution under constant stirring at room temperature (32 °C), until the reaction mixture attained pH 8.5. The precipitate obtained was separated by filtration and was washed free of sulphate ions (confirmed by the BaCl₂ test) with distilled water. The precipitate was further dispersed in 1000 ml of hot distilled water and was peptised by the addition of 10% HNO₃ (Merck, India Ltd) solution. A stable sol was obtained at a pH range 1.7 to 2.2. To the stable sol 1, 2, 5 and 10 mol % alumina is added as boehmite sol using Al(NO₃)₃. 9H₂O (sd Fine Chemicals, India Ltd) as a precursor, which was prepared by a procedure reported
earlier. To the undoped and alumina doped titania sol, 2 wt% polyethylene glycol was added. The resultant sol was coated on glass surfaces using a dipcoater machine (KSV dipcoater, Finland). Before the deposition, glass substrates were cleaned in concentrated sulphuric acid, distilled water and then absolute ethanol. TiO$_2$ thin film was deposited on substrate by a dip-coating process at room temperature with the withdrawing speed of about 2 cm/min. Substrates were immersed into the TiO$_2$ sol for 1 min. Upon withdrawing from the sol, the substrates were dried at 70 °C. The corresponding dried gels were further characterized using Thermogravimetric analyzer (Shimadzu, TGA 50H, Japan). The coated glass slides were calcined at 400 °C for 3 h at a heating rate 1 °C per min. XRD patterns of the calcined gels were taken in a Philips X' pert X-ray diffractometer in the diffraction angle 2θ range 20-60° using Cu Kα radiation. The crystallite size was calculated using Scherrer equation 4.2.1.

$$\Phi = \frac{K\lambda}{\beta \cos \theta}$$

(4.2.1)

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. The surface morphology of dried TiO$_2$ thin film was observed by a Scanning electron microscope (SEM JEOL JSM-6700F) and Atomic Force Microscope (Topometrix Inc.) in contact-mode using a silicon tip (Mikro Masch Inc., Estonia) of length: 350 μm, width: 10 μm, height: 1 μm, and an end-curvature radius < 10 nm. Spectroscopic analysis of the TiO$_2$ film was performed using UV-Visible spectrophotometer (Shimadzu UV 2401) in the wavelength range of 200–800 nm. The surface area measurements and pore size analysis were carried out by nitrogen adsorption using Micromeritics Gemini 2375 surface area analyser after degassing each sample at 200 °C for 2 h. Raman spectra of the samples was
taken using a FT- Raman spectrometer (Bruker IFS66V). Methylene blue degradation was used for the determination of photocatalytic property of titania film. In presence of titania film, methylene blue solution shows photo catalytic degradation. In a typical experiment, coated glass plates were dipped in an aqueous solution of methylene blue dye (AR Grade, Qualigens Fine Chemicals, India Ltd) for one hour. It was dried in dark, and irradiated with ultraviolet light in a UV chamber with wavelength range from 200 to 400 nm (Rayonet Photo reactor, The Netherlands). The degradation of the dye was monitored after 60 min using UV-Visible spectrometer (Shimadzu, Japan, UV-2401 PC).

4.2.4 Result and Discussion

4.2.4.1 Thermogravimetric analysis

Thermogravimetric analysis shows (Figure 4.2.1) that the coating solutions dried at 70 °C undergo three decomposition steps between the analysed temperature 30 to 1000 °C. Thermo gravimetric analysis curve shows similar decomposition patterns for pure titania coating solution and the 10 mol% alumina doped titania coating solution. But 10 mol% alumina doped titania coating solution shows slight increase in the total weight loss. Pure titania coating solution dried at 70 °C undergoes a total weight loss of 23%, whereas 10 mol% alumina doped titania coating solution results in a total weight loss of 27.5%. The weight loss below 150 °C is due to the removal of loosely bound water in the gel network. The decomposition step between 200 and 400 °C is due to the decomposition of nitrate ions, dehydroxylation of the gel and removal of the polyethylene glycol used in the coating solution. The % of weight loss is 15.4 and 16.6% respectively for titania and 10 mol% alumina doped titania compositions in the temperature range 200 to 400 °C. Weight loss between 400 and 1000 °C is extremely small and, hence, a lack of
clear decomposition step. The higher weight loss in titania–alumina samples may be due to the boehmite species incorporated in the titania gel network. The similarity in the decomposition pattern of alumina doped samples with pure titania may be an indication of the higher degree of homogeneous dispersion achieved between titania and alumina in the doped system through the mixing of the respective colloidal sols.

![Graph showing TGA curves for coating solution (a) titania (b) 10 mol% alumina doped titania.](image)

**Figure 4.2.1.** TGA curve of coating solution (a) titania (b) 10 mol% alumina doped titania.

### 4.2.4.2 X-ray diffraction analysis

The X-ray diffraction analysis (Figure 4.2.2) indicated that only anatase phase was present in pure and alumina doped titania samples. The crystallite size decreases with increase in the alumina content in the titania matrix (Table 4.2.1). It was 11.3 nm in pure titania and it decreases to 8.1 nm in case of 10 mol% alumina doped titania. The alumina in the titania matrix effectively hinders the crystallite growth of titania.
Figure 4.2.2. X-ray diffraction pattern of coating solution calcined at 400 °C for 1h (a) titania (b) 1 mol% alumina doped titania (c) 2 mol% alumina doped titania (c) 5 mol% alumina doped titania (d) 10 mol% alumina doped titania

Table 4.2.1 Crystallite size data of alumina doped titania

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>11.28</td>
</tr>
<tr>
<td>TiO₂ + 1 mol% Al₂O₃</td>
<td>10.78</td>
</tr>
<tr>
<td>TiO₂ + 2 mol% Al₂O₃</td>
<td>10.11</td>
</tr>
<tr>
<td>TiO₂ + 5 mol% Al₂O₃</td>
<td>10.04</td>
</tr>
<tr>
<td>TiO₂ + 10 mol% Al₂O₃</td>
<td>8.06</td>
</tr>
</tbody>
</table>

4.2.4.3 UV–Visible spectrophotometry

Pure and alumina doped titania thin films deposited on glass substrates calcined at 400 °C are transparent. The corresponding UV–Vis transmittance spectra and Tau plot
for band gap determination are provided in Figure 4.2.3. & 4.2.4. The bandgap against alumina content in the titania matrix for pure and alumina doped titania films calcined at 400 °C are provided in Figure 4.2.5. The titania film has a transmittance between 96 to 87% within the visible region (400 to 800 nm). A significant decrease in the transmittance below 400 nm can be assigned to absorption of light by anatase titania thin film. This leads to the excitation of electrons from the valence band to the conduction band of titania.\textsuperscript{55} UV-Visible spectra show that the adsorption edge was shifted to the lower wavelength region when the amount of alumina in the titania thin film increases. These observations indicate that the electronic structure of the overall solid is deeply modified. The UV-visible spectrum of titania coated glass looks like the typical one for anatase.\textsuperscript{55,56} It is characterized by an absorption edge whose high wavelength limit is detected with an absorption onset at 385 nm. This edge is associated with the electron transition from the O\textsubscript{2p} valence band to the Ti\textsubscript{3d} conduction band and it corresponds to an O\textsuperscript{2-} to Ti\textsuperscript{4+} charge transfer transition. The incorporation of aluminium causes a significant shift of the absorption edge towards lower wavelengths, as previously reported.\textsuperscript{57} These observations indicate that the electronic structure of the overall solid is deeply modified. This effect cannot be explained by a simple "dilution" or coverage of the anatase particles by alumina particles or "monolayers" and also cannot be due to a decrease of the particle size of titania, as proposed in the case of silica-titania.\textsuperscript{58} In fact, samples with very different particle sizes and surface areas is found to vary much less than in the present case. Moreover, the decrease of the crystal size as measured above is quite limited and is nil between the 2 mol% alumina doped titania and 5mol% alumina doped titania, which
instead shows a very different absorption edge shift. This effect must then be explained by dissolution of $\text{Al}^{3+}$ ions into the TiO$_2$ matrix.

Figure 4.2.3. UV-Visible spectrum of (a) Pure titania (b) 1 mol% Al$_2$O$_3$ doped TiO$_2$ (c) 2 mol% Al$_2$O$_3$ doped TiO$_2$ (d) 5 mol% Al$_2$O$_3$ doped TiO$_2$ (e) 10 mol% Al$_2$O$_3$ doped TiO$_2$

Figure 4.2.4. Tau plot of (a) Pure titania (b) 1 mol% Al$_2$O$_3$ doped TiO$_2$ (c) 2 mol% Al$_2$O$_3$ doped TiO$_2$ (d) 5 mol% Al$_2$O$_3$ doped TiO$_2$ (e) 10 mol% Al$_2$O$_3$ doped TiO$_2$
Figure 4.2.5. Band gap versus alumina content in the titania matrix

Accordingly, the Ti$_{3d}$ and the Al$_{3p}$ orbitals mix in the conduction band, and this causes the lower limit of the conduction band to shift up, so that the energy gap increases from near 3.22 eV to near 3.47 eV calculated by Tau plot method. Therefore, the observations from the UV-visible spectra of the samples strongly support the idea that part of the alumina actually dissolves into the anatase bulk giving rise to a solid solution.

4.2.4.4 Scanning Electron Microscopy

Figure 4.2.6. shows Scanning electron micrographs of the pure and alumina doped titania thin films deposited on glass slides calcined at 400 °C. It can be observed that in the pure titania thin film, the particles are grown in to a higher size than the alumina doped titania film. The homogeneously distributed alumina effectively hinder the particle growth of titania. It is already evident from the X-ray diffraction analysis that the crystallite size of all alumina doped composition is lower than the pure titania film.
Figure 4.2.6. Scanning Electron Micrographs of (A) undoped titania film (B) 10 mol% alumina doped titania film.

4.2.4.5 Atomic Force Microscopy

The surface structure of coating can be viewed from atomic force microscope (Figure 4.2.7). It shows that, for the pure titanium oxide coating, the particles are grown into large size than the 10mol% alumina doped titania. In the case of coating with addition of alumina, alumina will block the crystallite growth of titania thin film.

Figure 4.2.7. Atomic Force Micrographs of (A) undoped titania film (B) 10 mol% alumina doped titania thin film

As a result of alumina addition, titanium oxide remains less agglomerated, and the crystallization rate of titanium oxide is reduced, which was already observed from the
crystallite size data obtained from X-ray diffraction. The thickness of the titania layer formed on the glass surface was found out to be ~50nm.

4.2.4.6 BET specific surface area analysis

Textural characteristics of the pure and alumina doped titania thin film composition calcined at 400 °C were derived from N₂ adsorption analysis. Specific surface area ($S_{\text{BET}}$), total pore volume calculated at $p/p_0 = 0.9$, BJH mesopore volume and micro pore volume which were calculated by t-plot method and average pore diameter value are presented in Table 4.2.2. The adsorption isotherms (Figure 4.2.8) of all samples show type IV behaviour with the typical hysteresis loop. This hysteresis loop is characteristic of mesoporous materials and it infers that the mesoporous thin layer is formed on the glass substrate. Surface area results shows that all the doped titania samples have higher surface area than the undoped one after calcinations at 400 °C. In the case of pure titania it is 72 m²g⁻¹ and for 10 mol% alumina doped titania it is 152 m²g⁻¹ which is two times higher than the undoped titania. The total pore volume and mesopore volume increased as the alumina content in the titania matrix is increased.

Table 4.2.2. Textural characteristics of the pure and alumina doped titania thin film composition calcined at 400 °C derived from N₂ adsorption analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area ($m^2g^{-1}$)</th>
<th>Total pore volume ($cm^3g^{-1}$)</th>
<th>Average Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>72.33</td>
<td>0.1477</td>
<td>7.5</td>
</tr>
<tr>
<td>TiO₂ + 1 mol% Al₂O₃</td>
<td>87.5</td>
<td>0.1598</td>
<td>7.3</td>
</tr>
<tr>
<td>TiO₂ + 2 mol% Al₂O₃</td>
<td>95.8</td>
<td>0.1728</td>
<td>7.2</td>
</tr>
<tr>
<td>TiO₂ + 5 mol% Al₂O₃</td>
<td>125.0</td>
<td>0.1978</td>
<td>6.3</td>
</tr>
<tr>
<td>TiO₂ + 10 mol% Al₂O₃</td>
<td>152.4</td>
<td>0.2116</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Figure 4.2.8. Adsorption-desorption isotherm of (■) Pure titania (●) 1 mol% Al₂O₃ doped TiO₂ (▲) 2 mol% Al₂O₃ doped TiO₂ (▼) 5 mol% Al₂O₃ doped TiO₂ (♦) 10 mol% Al₂O₃ doped TiO₂

Figure 4.2.9. Pore size distribution curve of (■) Pure titania (●) 1 mol% Al₂O₃ doped TiO₂ (▲) 2 mol% Al₂O₃ doped TiO₂ (▼) 5 mol% Al₂O₃ doped TiO₂ (♦) 10 mol% Al₂O₃ doped TiO₂
The pore size distribution curve (Figure 4.2.9) shows that pores are in mesoporous region and as alumina content increases, the poresize shifted further to lower region, which indicates that the alumina in titania matrix effectively hinders the pore size growth. In adsorption isotherm there was no tailing upward at higher relative pressure and this shows the formation of long-range order mesoporosity without any contribution of large pores beyond mesopore scale (>50 nm).59

4.2.4.7 Raman spectroscopy

Figure 4.2.10 shows the Raman spectra of pure and 10 mol% alumina doped titania. The observed peaks at 151, 404, 513 and 634 cm\(^{-1}\) can be attributed to the characteristics of the anatase phase. This indicates that the anatase is the predominant phase structure. The maximum at low-frequency of the Raman band, provides an idea of the nanoparticle size, since the particle size can cause large shifts in the location of the raman peaks and their widths, namely, the quantum size confinement effect.60

**Figure 4.2.10.** Raman spectra of (a) undoped titania (b) 10 mol% alumina doped titania
The lowest frequency peak is at 151 cm$^{-1}$ for undoped titania. It can also be evidently seen that the width of this peak increased and resulted in blue shift to 160 cm$^{-1}$ in the case of 10 mol\% alumina doped titania. This is due to the lower crystallite size of the sample than the undoped titania.$^{61}$

4.2.4.8 Photo catalytic activity studies

Photoactivity of the titania film was measured using methylene blue degradation studies. The photocatalytic activity of pure titania and titania doped with alumina coatings was studied using the methylene blue degradation technique. Methylene blue shows considerable degradation in presence of titania coating. The degradation was followed through UV spectral measurement. The efficiency of degradation of methylene blue was plotted against alumina content in titania and is given in Figure 4.2.11. It was observed that upto 2 mol\% alumina doping, the photoactivity increases and then decreases as the doping concentration of alumina is increased.

![Graph](image)

**Figure 4.2.11.** Methylene blue degradation efficiency against alumina concentration in titania matrix.
The excessive doping makes the space charge layer very narrow so that the penetration depth of light into TiO$_2$ greatly exceeds the thickness of the space charge layer, resulting in easy recombination of electron-hole pairs and poor photoactivity.\textsuperscript{62} This may be one of the reasons for the lower activity of 5 and 10 mol\% aluminium doped titania.

4.2.5 Conclusions

An aqueous sol-gel method was developed for the preparation of alumina doped titania thin film. X-ray diffraction analysis indicates that the anatase layer was formed on the glass surface. Titania coatings having transmittance between 85 to 95\% were developed on the glass surface using dip coating technique. The alumina addition leads to increase in band gap. Scanning electron micrographs indicates that a uniform thin layer of titania coating was formed on the glass surface. Atomic force micrographs indicate that undoped titania particles were grown into larger size than the 10 mol\% alumina doped titania. The thickness of the coating was \~50 nm. Mesoporous nature of the titania layer formed was evident from BET surface area analysis. The pore stability was achieved by alumina doping. Raman spectra were used to confirm the exclusive presence of anatase phase in the coatings. The coated surface was photocatalytic and the alumina doped sample showed higher activity than the undoped one. The present method is hence very useful for the preparation of photocatalytic surfaces from a cheaper precursor, which will enable the bulk production of photocatalytic titania surfaces.
4.6 References


59. S. J. Gregg, K. S. W. Sing, *Adsorption, Surface area and Porosity, 2nd Ed.*, Academic Press, **1982**.

