CHAPTER III

EXPERIMENTAL DETAILS
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EXPERIMENTAL

3.1. The chemicals used in this study are given below;

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Make</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium tetraisopropoxide (TTIP)</td>
<td>Sigma Aldrich</td>
<td>Precursor for TiO₂</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>Merck</td>
<td>To digest TTIP</td>
</tr>
<tr>
<td>Phosphomolybdic acid</td>
<td>Fischer</td>
<td>Catalyst</td>
</tr>
<tr>
<td>Phosphotungstic acid</td>
<td>Fischer</td>
<td>Catalyst</td>
</tr>
<tr>
<td>Copper based POM</td>
<td>(Synthesised)</td>
<td>Catalyst</td>
</tr>
<tr>
<td>Tungsten based POM</td>
<td>(Synthesised)</td>
<td>Catalyst</td>
</tr>
</tbody>
</table>

Indium Tin Oxide (ITO) conducting glass (70 - 100 Ω/cm²) plate was purchased from Sigma-Aldrich and used for the coating of film by electrodeposition method.

High pure water was obtained from TKA-LAB Reinst system and used to make solutions.

For the electrodeposition process, supporting electrolytes were needed at different pH conditions. Supporting electrolyte of acidic pH 1 was obtained by the addition of 50 ml of 0.2 M KCl and 134 ml of 0.2 M HCl and made up to 200 ml with water. Supporting electrolyte of neutral pH 7 was obtained by the addition of 7.5 g KCl and made up to 1000 ml with water. Supporting electrolyte of alkaline pH 13 was obtained by the addition of 50 ml 0.2 M KCl and 132 ml 0.2 M NaOH and made up to 200 ml with water.
3.2. Procedure for the synthesis of TiO$_2$

TiO$_2$ nanoparticles were synthesised by the hydrolysis and condensation of titanium tetraisopropoxide as the precursor. The synthesis was carried out by three different conditions;

(i) synthesis at room temperature: to the 1 ml of TTIP, 20 ml of water was added and the mixture was kept under constant stirring on a magnetic stirrer for 5 h at room temperature. The product thus obtained as powder was filtered and dried. This sample is designated as S$_1$.

(ii) synthesis at 70°C in water: to the 1 ml of TTIP, 20 ml of water was added and stirred on a magnetic stirrer for 5 h at a temperature of 70°C. The product thus obtained as powder was filtered and dried. This sample is designated as S$_2$.

(iii) synthesis at 70°C in nitric acid: to the 1 ml of TTIP, 20 ml of 0.1M nitric acid was added and stirred for 5 h at 70°C. The product thus obtained as powder was filtered and dried. This sample is designated as S$_3$.

Surfactants were not used in the synthesis. The sample S$_1$ was aged for a week at room temperature under atmospheric pressure. The powders obtained by the said methods were calcinated in an electric furnace at a temperature of 400°C for 2 h as reported by Zaine [1].

3.3. Procedure for the preparation of TiO$_2$ film

The preparation of TiO$_2$ film was performed through three steps; (i) synthesis of TiO$_2$ sol, (ii) electrodeposition of sol on ITO plate and (iii) annealing. In the synthesis of TiO$_2$ sol, nitric acid at two different concentrations (0.1 M and 0.5 M) was used. 1 ml of titanium tetraisopropoxide was slowly dropped in to 20 ml of nitric acid and stirred vigorously for
3 h at a temperature of 70°C as reported by Tipparach et al. [2]. Electrodeposition was performed using CHI-620A instrument with a three electrode setup. Cleaned ITO plate as the working electrode, platinum foil as the counter electrode and Ag/AgCl as the reference electrode were used. Prior to the electrodeposition of film, the ITO substrate was thoroughly cleaned with acetone and kept in an oven at 100°C for 15 min. The coating solution comprised of 10 ml sol and 1 ml supporting electrolyte solution. Anodic electrodeposition was carried out at a selected potential of 1.0 V for 30 min, which led to the formation of TiO(OH)\_2\cdot xH\_2O gel film on the ITO electrode. After the deposition step, the film thus formed was washed with distilled water and dried at 100°C for 10 min. TiO\_2 film thus deposited on ITO plate was annealed at different thermal conditions (room temperature, 200°C, 300°C and 400°C) for 2 h and the products thus obtained are designated as T\_1, T\_2, T\_3 and T\_4 respectively.

### 3.4. Procedure for the synthesis of TiO\_2-POM film

Four different photocatalysts were synthesized using TiO\_2 and four different POMs; (i) phosphomolybdic POM (designated as P\_1), (ii) phosphotungstic POM (designated as P\_2), (iii) Copper based POM (designated as P\_3) and (iv) tungsten based POM (designated as P\_4). P\_1 and P\_2 were of commercial grades and used as such. P\_3 and P\_4 were synthesized as per the procedures supplied by Dr. Monika Goral of Poland. The technical details are not provided here for the purpose of patenting / Intellectual property right issue.

The preparation of TiO\_2-POM composite film was performed through three steps; (i) synthesis of composite sol, (ii) electrodeposition of sol on ITO plate and (iii) annealing. For step (i), 1 ml of TTIP was slowly dropped in to 20 ml of 0.5 M nitric acid and stirred vigorously for 2 h at 70°C. To this, 0.6 g of POM (P\_1 / P\_2 / P\_3 / P\_4) was added and stirred over a magnetic stirrer for 1 h at 70°C. In step (ii), electrodeposition was performed using
the said instrument with standard procedure. After the deposition, the composite film thus formed was washed with distilled water and dried at 100°C for 10 min. Finally the ITO plate containing TiO₂-POM composite film was annealed at 400°C for 2 h. The composite films thus obtained (i) with phosphomolybdic POM is designated as P₁T, with phosphotungstic POM is designated as P₂T, (iii) with copper based POM is designated as P₃T and (iv) with tungsten based POM is designated as P₄T.

3.5. Material characterisation

TiO₂ powder, TiO₂ film and four different TiO₂-POM composite materials were subjected to characterisation by various instrumental analyses. X-ray diffraction (XRD) measurements were performed using X'Pert-PRO X-ray diffractometer; samples were analysed in the range between 10 and 80° as 2θ and Cu as anode (K-Alpha -1.54060 Å). Fourier transform infrared (FT-IR) spectra were recorded using Shimadzu 8400S spectrometer. Scanning electron microscopy (SEM) images were obtained with HITACHI S3000H instrument. Transmission electron microscopy (TEM) was employed to determine the particle size with JEOL-JEM-2100 instrument operating at 200 kV. UV-Vis diffuse reflectance spectra (DRS) were obtained with Shimadzu UV-3101PC spectrophotometer equipped with an integrating sphere and BaSO₄ as a reference. The surface morphology was assessed with atomic force microscope (AFM) at tapping mode with a Nanoscope III Digital-VEECO (E type scanner, 512×512 pixels, with scanned size 500 nm×500 nm). Photoluminescence (PL) spectra of the samples were obtained in the range from 300 to 900 nm using excitation line at λ = 300 nm with FluoroMax-3, Jobin-Yvon-Horiba PL-system. Jasco V-530 spectrophotometer was used for the UV-Vis absorbance analysis.
3.6. Photocatalytic decolourisation of dyes

The photocatalytic decolourisation efficiency of TiO$_2$ powder, TiO$_2$ film and TiO$_2$-POM films were tested with Reactive Red 2 (RR2) dye and Disperse Yellow 231 (DY231) dyes. The technical details of the dyes are given below;

**Structure of RR2**

![Structure of RR2](image)

- **M.F**: C$_{19}$H$_{10}$C$_{12}$N$_6$O$_7$S$_2$2Na
- **C.I. Number**: 18200
- **CAS Number**: 17804-49-8
- **IUPAC name**: 2,7-Naphthalenedisulphonicacid,5-[4,6-dichloro-1,3,5-triazin-2-yl]amino]-4-hydroxy-3-(2-phenyl diazenyl)-disodium salt

**Structure of DY231**

![Structure of DY231](image)

- **M.F**: C$_{25}$H$_{22}$N$_4$O$_4$
- **C.I. Number**: 128500
- **CAS Number**: 143067-35-0
- **IUPAC name**: benzyl 4-[(2Z)-2-(1-butyl-5-cyano-4-methyl-2,6-dioxo-1,6-dihydropyridin-3(2H)-ylidene)hydrazinyl] benzoate; benzyl 4-[(1-butyl-5-cyano-2-hydroxy-4-methyl-6-oxo-3-pyridyl)azo] benzoate.
Effects of different photocatalysts, pH, dye concentration and treatment time were studied. The photocatalytic activity of TiO$_2$ powders synthesized by three different methods was used for dye decolourisation. Reactive Red 2 and Disperse Yellow 231 dyes were taken as model pollutants. Stock solution containing $10^{-4}$ M dye was prepared with water. In each experimental test, 10 ml dye solution was taken in a beaker and 5 mg of TiO$_2$ powder ($S_1$) was added. To this, required volume of appropriate pH solution was added to bring the final volume to 100 ml. This solution was stirred for 10 minutes in the dark to attain equilibrium of adsorption and desorption process of the dye with TiO$_2$ nanoparticles and irradiated after stirring. Warm soft light (visible) having wavelength greater than 370 nm with colour temperature of 3000K UV-A lamp was used as photolight source. The mixture containing dye solution and photocatalyst was stirred for 120 minutes and then spectral absorption was determined. This procedure was adopted for $S_2$ and $S_3$ samples.

The photocatalytic activity of TiO$_2$ film and TiO$_2$-POM composite films were studied with the said procedures. The photocatalytic efficiency was calculated using UV-vis spectral absorbance of the test dye solution before and after the photocatalytic activity. Effect of pH was studied at different conditions such as 1, 7 and 13. The decolourised dye solutions were collected and subjected to chemical oxygen demand (COD) test. For this, 0.3 ml COD solution A (Art.no.1.14538) and 2.3 ml COD solution B (Art.no.1.14680) were taken in a cell and mixed; then 3 ml of test dye solution was added to the cell, the lid was closed and the cell content was digested using Merck Thermoreaktor TR200 set up at 148°C for 2 h. In another cell, 0.3 ml COD solution A, 2.3 ml COD solution B and 3 ml of water were added and considered as ‘blank’. The lid was closed, digested for 2 h, cooled and the spectral absorbance was measured at a wavelength of 585 nm against the blank and multiplied with a factor 1636 to get the COD value in ppm or mg/L.
References
