CHAPTER 4

HIGH TEMPERATURE MICROWAVE ASSISTED SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS CRYSTALLINE TITANIA

4.1 INTRODUCTION

Synthesis of mesoporous metal oxide materials such as SnO$_2$ and TiO$_2$ has been receiving increasing attention of researchers from various fields due to its potential as solar cells, sensors and catalytic membranes (Kresge et al 1992; Taguchi and Schuth 2005; Zhang et al 2003; Zhao et al 2007). In 1995, mesoporous TiO$_2$ was first prepared by using alkyl phosphate surfactants as template and titanium isopropoxide as a titanium source (Antonelli et al 1999). Subsequently, several synthesis techniques have been proposed to achieve mesoporous TiO$_2$ including sol-gel, templating, hydro and solvothermal, ultrasound-induced method ion liquid, and evaporation-induced self-assembly methods (Tan et al 2003; Wang et al 2001; Soller-Illia et al 2002; Yu et al 2002; Yoo et al 2005; Su et al 2006; Jiao et al 2007; Li et al 2007). These materials with a well-defined pore size, porosity, high specific surface area and excellent band structure make them very special and attractive (Chen et al 2007; Yang et al 2007).

Recently, application of microwave irradiation in synthetic chemistry has become an attractive synthetic method since its first report in 1986 (Geyde et al 1986). Microwave heating in synthetic chemistry is considered to be volumetric heating. It is advantageous because it maintains
molecular homogeneity, provides rapid heating rate resulting in reduction of reaction time by orders of magnitude. Due to its high product efficiency, volumetric heating, short reaction time and energy economy, materials with better properties than those obtained by using conventional heating methods can be achieved. As a result, it has opened up the possibility of realizing new reactions in a very short time and wide application in the synthesis of organic and inorganic materials, although it is still less explored in inorganic material synthesis (Motuzas et al 2005; Tian 2008; Cundy and Cox 2003).

In this work, we demonstrate the rapid synthesis of mesoporous TiO\(_2\) with nanocrystalline architecture at a higher temperature employing microwaves. By making use of various characterization techniques such as XRD, nitrogen adsorption, HRTEM, UV-Vis DRS, HRSEM and photoluminescence it is being proposed that the microwave irradiation effectively reduces the synthesis time and promotes the growth of mesoporous TiO\(_2\) material with excellent structural and textural properties as compared to those obtained from conventional synthetic methods.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Synthesis of Mesoporous TiO\(_2\)

Triblock copolymer (Pluronic P123 (EO\(_{20}\)PO\(_{70}\)EO\(_{20}\)), molecular weight = 5800) from Sigma Co. was used as the structure directing agent; titanium tetraisopropoxide (TIP) (Aldrich), acetic acid and ethanol were used as received without further purification. They were taken in a reaction vessel and stirred for 40 mins. Deionized water (40 g) was added and stirring was continued for another 1 h. The resulting aqueous solution taken in a Teflon vessel was treated inside a microwave oven at 130 °C for 2 h. The product was collected by filtration, washed thrice with deionized water followed by washing with ethanol and finally kept for drying at 100 °C overnight. The synthesized material was calcined in air at 400 °C for 4 h to remove the template.
4.2.2 Characterization

The powder X-ray diffraction patterns of TiO$_2$ samples were collected on a Rigaku diffractometer using CuK$\alpha$ ($\lambda = 1.5406 \text{ Å}$) radiation. The diffractograms were recorded in the 2θ range of 0.7-10° with a 2θ step size of 0.01° and a step time of 6 s. Nitrogen adsorption and desorption isotherm was measured at -196 °C on a Quantochrome Autosorb 1 sorption analyzer. The sample was outgassed for 3 h at 250 °C under vacuum in the degas port of the adsorption analyzer. The specific surface area was obtained from the adsorption branch of the isotherm in the relative pressure range of 0.05-0.18 using the BET equation.

The HRTEM image was obtained with TEM JEOL JEM-2000EX2. The preparation of sample for HRTEM analysis involved sonication in ethanol for 5 min and deposition on a copper grid. The sample was imaged at an accelerating voltage of 200 kV. The morphology and elemental mapping of the materials were observed on a Hitachi S-4800 field emission scanning electron microscope (HR-FESEM) with energy-dispersive X-ray (EDS) spectroscopy using an accelerating voltage of 10 kV. The UV-Visible diffuse reflectance spectrum (UV-vis DRS) was measured with a Perkin-Elmer Lambda 18 spectrometer equipped with a Praying-Mantis diffuse reflectance attachment. BaSO$_4$ was used as reference. The photoluminescence (PL) spectrum was measured at room temperature in a spectral range of 400-800 nm using a Xe lamp with a wavelength of 325 nm as the excitation source.

4.3 RESULTS AND DISCUSSION

4.3.1 Powder X-ray Diffraction

The mesostructural order of the both as-synthesised and calcined mesoporous TiO$_2$ prepared by the microwave-assisted high temperature
process was analysed by powder XRD pattern. Figure 4.1 represents the low-angle XRD patterns of both the as-synthesized and calcined mesoporous TiO$_2$ samples. Both the calcined and as-synthesized samples show a peak at lower angle, indicating that the samples possess ordered mesoporous structure. It is quite interesting to note that the intensity of the (100) peak of the calcined sample is much higher than that of the as-synthesized sample. This could be due to the fact that the unreacted Ti(OH)$_4$ species are condensed during the calcination process which helps to enhance the structural order of the materials.

![Graph showing XRD patterns](image)

**Figure 4.1** Lower-angle powder XRD patterns of mesoporous TiO$_2$ materials (a) as-synthesized and (b) calcined
The wide-angle XRD patterns of the both as-synthesized and calcined sample are shown in Fig. 4.2. The numerous higher order reflections with a high intensity obtained for the calcined TiO$_2$ sample is a clear indication of its higher crystalline nature. However, only broad peak with a low signal to noise ratio was observed for the as-synthesized sample. After calcination process, the higher order reflections become sharp and intense indicating that calcination of the as-synthesized sample under O$_2$ atmosphere at 400 °C resulted in the formation of highly crystalline stable oxide with an ordered mesostructure. The higher order reflections (101), (004), (200) and (204) at the respective 2θ values of 25.27, 37.93, 48.01 and 62.70 correspond to the crystal planes of (101) (004) (200) and (204) of anatase TiO$_2$. It is quite an interesting observation that the microwave treatment favours the formation of crystalline structure with anatase phase unlike most of the
conventional synthetic methods. The crystallite size of the calcined mesoporous TiO$_2$ calculated using Scherrer formula applying the full width half maximum (FWHM) of the (101) peak is found to be 8.2 nm.

4.3.2 BET Analysis

Figure 4.3 represents the nitrogen adsorption isotherm of the calcined mesoporous TiO$_2$ sample outgassed at 250 °C for 3 h prior to the BET measurement. The isotherm exhibits a type IV pattern with sharp capillary condensation step of nitrogen adsorbed volume ($P/P_0$) at about 0.40 and a H1 hysteresis loop, indicating the presence of mesopores in the calcined sample. The specific surface area and pore volume of the mesoporous TiO$_2$ determined from the nitrogen adsorption-desorption isotherm are found to be 118 m$^2$/g and 0.180 cm$^3$/g respectively.

![Nitrogen adsorption-desorption isotherm of calcined mesoporous TiO$_2$](image)

**Figure 4.3** Nitrogen adsorption-desorption isotherm of calcined mesoporous TiO$_2$

The pore diameter of the calcined mesoporous TiO$_2$ calculated from the Barret-Joyner-Halenda method was found to be 3.1 nm.
4.3.3 UV–Vis spectroscopy

Figure 4.4 depicts the UV–vis absorption spectra of both as-prepared and calcined mesoporous TiO$_2$. The bandgap energies of these materials were found from the intercepts of the tangents in the $(\alpha h\nu)^2$ versus excitation energy plot. It was observed that optical band gap of as-prepared material was 3.08 eV which increased to 3.12 eV for the calcined material. This increase may be attributed to the increase in the degree of crystallinity and the change of the crystalline phase. It is quite clear that the crystallite size of the as-synthesized sample is much larger than that of the crystallite size due to the uncondensed Ti(OH)$_4$ species.

During the calcination process, the unreacted Ti(OH) species undergo condensation process which leads to the framework contraction. As a result, the crystallite size of the calcined sample is significantly reduced, resulting a blue-shift of the absorption edge. We also surmise that the transformation of the phase from rutile to anatase during the calcination process may also be responsible for the rise in the bandgap of the calcined samples. It is found that the intensity of the peak is much lower for the calcined sample than that of the as-synthesized sample. It is also interesting to note that both the as-synthesized and calcined samples show peaks around 230 nm and 320 nm which may be attributed to the electron migration between tetrahedrol coordinated Ti and O and the octahedrally coordinated Ti and O, respectively, originating from the anatase TiO$_2$ phase.
Figure 4.4 UV-Vis DRS spectrum of mesoporous TiO$_2$ materials (a) as-synthesized and (b) calcined

4.3.4 Surface Morphology and Composition Analysis

Figure 4.5 displays the SEM images of both as-synthesized and calcined TiO$_2$ samples. It is observed that both as-synthesized TiO$_2$ and calcined TiO$_2$ are composed of a large quantity of relatively uniform particles with an average diameter of about 1.5 mm. It should also be noted that the particles become smaller after the calcination process without affecting the morphology, which is quite consistent with the data obtained from the UV-Vis DRS.
Figure 4.5 HR-SEM images of mesoporous TiO$_2$ materials (a) as-synthesized and (b) calcined

Figure 4.6 shows the EDS pattern of the calcined sample. The sample shows the peak corresponds to Ti and O. The absence of the C peak in the pattern for the calcined sample clearly shows that the final product is free from the template used for its synthesis.

Figure 4.6 HRSEM-EDS pattern of calcined mesoporous TiO$_2$
4.3.5 High Resolution Transmission Electron Microscopy (HRTEM) Studies

Figure 4.7 shows the representative HR-TEM image of the calcined mesoporous TiO₂. The sample shows uniform size and shapes of TiO₂ nanoparticles with well ordered array of mesopores. The pores are arranged in a regular interval and highly ordered with a hexagonal honeycomb like structure. The pore size calculated from the TEM image is almost close to that obtained from the nitrogen adsorption isotherm. The clear diffraction ring shows the formation of well crystallized phase which is consistent with the wide-angle XRD pattern of the heated sample.

![HR-TEM image of calcined mesoporous TiO₂](image)

Figure 4.7 HR-TEM image of calcined mesoporous TiO₂ (Inset: selected area diffraction (SAED) pattern)

4.3.6 Photoluminescence Spectroscopy

Photoluminescence (PL) and excitation spectrum of the TiO₂ nanoparticles was recorded at room temperature to investigate the electron
transfer behaviour of the material over photo-generated electrons and holes. Fig. 4.8 shows the photoluminescence spectrum of the calcined mesoporous TiO$_2$ sample. The emission spectrum possesses a weak, broad band having peaks at 412, 449, and 469 nm which could be attributed to electron transition mediated by crystalline defects such as oxygen vacancies (Vanheusden et al 1996). These oxygen vacancies may act as radiative centers in luminescence processes (Gu et al 2004) and may be originated during the calcination process. As high calcination temperature was used for removing the template molecules from the porous matrix of the TiO$_2$, the exothermic reaction which generates high heat might create defect sites in the crystalline Ti-O-Ti framework. We surmise that these vacancies suppress the electron transfer and create a broad band in the spectrum.

![Photoluminescence spectrum of calcined mesoporous TiO$_2$](image.png)

**Figure 4.8 Photoluminescence spectrum of calcined mesoporous TiO$_2$**