PREPARATIONS AND CHARACTERIZATION OF WOLFRAM DOPED PHOTOCATALYST WITHMESOPOROUS TITANIUM DIOXIDE (TiO$_2$) VIA A SOL-GEL METHOD

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ABSTRACT

For the past two decades, the research of titanium dioxide was widely developed. The purpose of this study is to synthesize and characterize wolfram doped photocatalyst with mesoporous titanium dioxide (TiO_2) via sol-gel method. The pristine mesoporous titanium dioxide ($M-TiO_2$) and the doped mesoporous titanium dioxide (doped $M-TiO_2$) were successfully prepared as photocatalysts via a sol–gel method. Surfactant of hexadecyltrimethyl ammoniumbromide (CTAB) was used as a template. The mesoporous titanium dioxide was doped with wolfram (W). Those mesoporous photocatalysts ($M-TiO_2$ and doped $M-TiO_2$) were characterized using thermogravimetric analysis (TGA), X-ray diffraction (XRD) and specific surface area analysis (BET). As a result, XRD showed the doped $M-TiO_2$ had smaller particle size compared to $M-TiO_2$ and commercialize titanium dioxide (P-25). For TGA, all the mesoporous titanium dioxides were thermodynamically stable. Besides, in BET, the surface area of doped $M-TiO_2$ increase while the pore size decrease. The performances of the synthesized photocatalysts were measured by the degradation rate of methylene blue using an UV irradiating light of 365 nm by UV–visible spectrometer (UV-vis). The performances for the synthesized mesoporous titanium dioxides (the $M-TiO_2$, and the doped $M-TiO_2$) were much better than P-25. The doped $M-TiO_2$ acts better as a photocatalyst rater than pristine $M-TiO_2$. Doping wolfram in the $M-TiO_2$ promoted the increase of crystal size and bandgap values of the anatase TiO_2.

ABSTRAK

Bagi dua dekad yang lalu, penyelidikan titanium dioksida telah dibangunkan secara meluas. Tujuan kajian ini adalah untuk mensintesis dan menganalisa fotokatalis Wolfram didopkan dengan mesoporos titanium dioksida (TiO_2) melalui kaedah sol-gel. Titanium dioksida mesoporos asli (M-TiO_2) dan titanium dioksida didopkan mesoporos (didopkan M-TiO_2) telah berjaya disediakan sebagai fotokatalis melalui kaedah sol-gel. Surfaktan ammoniumbromide hexadecyltrimethyl (CTAB) telah digunakan sebagai templat. Titanium dioksida mesoporos telah didopkan dengan Wolfram (W). Kesemua fotokatalis mesoporos (M-TiO_2 dan didopkan M-TiO_2) telah dicirikan menggunakan analisis thermogravimetric (TGA), pembelauan sinar-X (XRD) dan analisis kawasan permukaan tertentu (BET). Hasilnya, XRD menunjukkan didopkan M-TiO_2 mempunyai zarah yang lebih kecil dari segi saiz berbanding M-TiO_2 dan komersial titanium dioksida (P-25). Bagi TGA, semua titanium dioksida mesoporos adalah stabil secara termodinamiknya. Selain itu, melalui BET, kawasan permukaan terdop M-TiO_2 meningkat manakala pengurangan saiz liang berlaku. Prestasi fotokatalis disintesis diukur oleh kadar penurunan metilena biru menggunakan sinaran cahaya UV penyinaran 365 nm oleh spektrometer UV-kelihatan (UV-vis). Prestasi titanium dioksida disintesis mesoporos (M-TiO_2, dan didopkan M-TiO_2) adalah jauh lebih baik daripada P-25. M-TiO_2 didopkan bertindak lebih baik sebagai fotokatalis daripada M-TiO_2 asli. Wolfram yang didop M-TiO_2 menggalakkan peningkatan saiz kristal dan nilai jurang kuasa anates TiO_2.

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Å	Angstrom
D	Mean grain size
β	Line broadening
k	Crystallite shape factor
λ	Radiation wavelength
θ	Bragg angle
P/P_0	Relative pressure
p	Pressure

LIST OF ABBREVIATIONS

TiO_2	Titanium dioxide
P-25	Commercialized Titanium dioxide anatase nano powder
$M\text{-}TiO_2$	Pristine mesoporous titanium dioxide
Doped $M\text{-}TiO_2$	Doped mesoporous titanium dioxide
XRD	X-ray diffraction
TGA	Termal Gravimetric Analysis
BET	Brunauer-Emmett-Teller (BET) Surface Area Analysis
UV-Vis	UV-Visible spectroscopy
CTAB	Hexadecyltrimethyl ammoniumbromide
TTIP	Titanium isopropoxide
W	Wolfram

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Titanium dioxide which is also known as titanium (IV) oxide or titania is the naturally occurring oxide of titanium with chemical formula of TiO_2. Titania is a very versatile material with attractive applications such as in production of capacitors, solar cells and also pigment in paintings (Di Paola et al., 2008).

Titanium dioxide (TiO_2) provides high chemical stability, high resistance to deteriorate in acid or alkali, furthermore with the advantage of being non-poisonous, safe, easy to be made, low cost and strong oxidation–reduction reactions. It also facilitates the decomposition of organic pollutants by light, resulting in generating non-poisonous CO_2, H_2O and some inorganic products. It restrains virus activity, catches and eliminates the planktons in the air, and provides the function of anti-pollution, deodorization, dust-proof, and self-clean. It thus becomes a popular photocatalyst material (Verma et al., 2006).

However, because of its band gap energy, TiO_2 utilizes only a very small fraction of the solar spectrum and thus doping with transition metals has been so far employed to extend the light absorption to the visible region. Doping with metals or metal oxides give two advantages which are firstly, it can reduce the band gap energy and then shift the absorption band to the visible region and secondly, metals can provoke a decrease in electron-hole recombination rate, acting as electron traps (Venkatachalam et al., 2007).

There are three structures for titanium dioxide: octahedrite, rutile, and brookite. All of them may be found at room temperature (Grant et al., 1959). However, octahedrite will turn to be rutile at 500–700 °C, thus rutile is the most thermodynamically stable. The octahedrite type has better chemical properties and photon characteristics, due to its good absorbability and lower electron/holes recombining rate (Sakai et al., 1993).

The energy gap of pristine titanium dioxide for photocatalysts is up to 3.2 eV, hence only the ultraviolet excitation (wavelength < 380 nm) can overcome this energy gap for electrons to jump to conduction band to form the electrons–holes pair. The formed holes in the surface of catalyst are used to deteriorate the organic materials or undesired pollutants before they re-combined with electrons (Kim et al., 2011).

Therefore, total surface area of catalyst plays an important role in the capability of deterioration. On other hand, the ultraviolet is only a small part (no more than 5%) in the sunlight. If a catalyst is fabricated with a lower energy gap, the excitation source used to generate the electrons–holes pair should shift to the visible light. It thus enhances the capability of deterioration, and will be very convenient for us (Tahiri et al., 1996).

In order to lower the energy gap of titanium dioxide, three approaches had been taken including metal atom doping, metal ion doping, and mixing with other semiconductors (Thomson et al., 1995). The reaction rate of photocatalysts doping metal is twice as much as that of the pristine titanium dioxide. The activity of titanium dioxide is related to the extension of the resulting declination time of the excited electrons by doping the metal ions into the titanium dioxides.

The metal ions may transfer electrons to the surface of the titanium dioxides by mean of trapping and de-trapping, and then to react with reactant thereon. Amount of added metal ions plays an important role in the process of electron transfer. When excess amount of the metal ions is added, the distance between the ions becomes closer, and the

recombination rate of electrons with holes thus enhances, thereby decreasing the photo-activity of the modified titanium dioxides (Hoffmann et al., 1995).

Present commercialized photocatalysts generally bear small surface area, resulting in a poor efficiency in absorbing and decomposing pollutant. Efficiency in absorbing and decomposing pollutant will be substantially increased if the photocatalysts are in the mesoporous structure (Marci et al., 1996). It is attributed to the large surface area of mesoporous structures, thereby facilitating the absorption of pollutant and its decomposition. Mesoporous titanium dioxide (M-TiO$_2$) can be obtained by using surfactant and polymer as the template (Yang et al., 1998).

1.2   Problem Statement

In recent years, titanium dioxide has been extensively used as an environmentally harmonious and clean photocatalyst due to its various qualities such as optical properties, low cost, high photocatalytic activity, chemical stability and also nontoxicity. However, its practical application becomes limited because of several reasons which are the low photon utilization efficiency as well as the need to use the Ultraviolet (UV) as an excitation source (Zhang et al., 1998).

Pure TiO$_2$ exhibits low photocatalytic property because of rapid recombination of photo-activated electrons and holes.   In order to solve these problems, the modification of these catalysts has also been done by doping them with metal. Doping with metal or metal oxide leads to the improvement of photocatalytic activity and disinfection effect (Mills et al., 1997).

The titanium dioxide (TiO$_2$) powder (P-25), which is a standard material in the field of photocatalytic reactions, includes anatase and rutile phase. It has been widely investigated since it can be used in many important fields such as in the environmental photocatalytic degradation of organic compound in waste water and also utilization of

solar energy. The effect of doping other transition metals is to change the equilibrium concentration of electrons or holes.

It has been known that the advantage of the doping of the metal ions in TiO_2 is the temporary trapping of the photogenerated charge carriers by the dopant and the inhibition of their recombination during migration from inside of the material to the surface or the enhanced association of the functionalized organic pollutants to the doping ion surface sites. The doping of transition metal ions may significantly influence the optical properties of TiO_2 photocatalyst, and the light absorption band of $M-TiO_2$ can be shifted into the visible region (Pozzo et al., 1999).

Referring to the methods, sol-gel method was used to synthesize mesoporous titanium dioxides. The metal ions may transfer electrons to the surface of the titanium dioxides by mean of trapping and de-trapping, and then to react with reactant thereon. Amount of added metal ions plays an important role in the process of electron transfer. When excess amount of the metal ions is added, the distance between the ions becomes closer, and the recombination rate of electrons with holes thus enhances, thereby decreasing the photo-activity of the modified titanium dioxides.

This research is focus on the preparation of a novel titanium dioxide with mesoporosity, referred to as mesoporous titanium dioxide, by a sol–gel method using hexadecyltrimethyl ammoniumbromide (CTAB) as the template. It is expected to increase the total surface of the catalyst, and hence the capability of deterioration. Additional, wolfram (W) was doped in $M-TiO_2$ to weaken the energy gap of catalyst, thereby shifting the excitation source from the ultraviolet to the visible light (Lachheb et al., 2002).

1.3 Objective of the Study

i) To synthesized the pristine mesoporous titanium dioxide (M-TiO₂) and doped mesoporous titanium dioxide (doped M-TiO₂) via a sol-gel method.

ii) To characterized samples using thermogravimetric analysis (TGA), X-ray diffraction (XRD) and specific surface area analysis (BET).

iii) To study the degradation of methylene blue via photocatalytic process using UV-visible spectrum analysis (UV-vis).

1.4 Scope of the Study

This study was aimed to prepare and characterize the novel photocatalyst with mesoporous titanium dioxide via sol gel method. The scope was to get mosoporous material where mesoporous material is a material containing pores with diameters between 2 and 50 nm [16]. Photocatalytic degradation of methylene blue was analyzed to measure the performance of the synthesized mesoporous titanium dioxides. The photocatalytic activity of the mesoporous TiO₂ sample was investigated by measuring the degradation of methylene blue (MB) with UV-irradiation, and compared with that of commercialized titanium dioxide anatase nano powder P-25.

1.5   Outline of the Study

This dissertation illustrates the information concerning the synthesis, characterization and photocatalytic activity of different metal-doped titania systems. Chapter 1 elucidates the background of the study and the current issue of titania as a photocatalyst. Chapter 2 presents the literature review that contains detail information about the whole research. Chapter 3 describes the research methodology that includes synthesis, characterization and photocatalytic activity of synthesized mesoporous titanium dioxides. Flowchart of research methodology was shown in figure. Chapter 4 explains results and discussion of the synthesized mesoporous titanium dioxides. Finally, chapter 5 summarizes the results obtained with recommendation for future work.
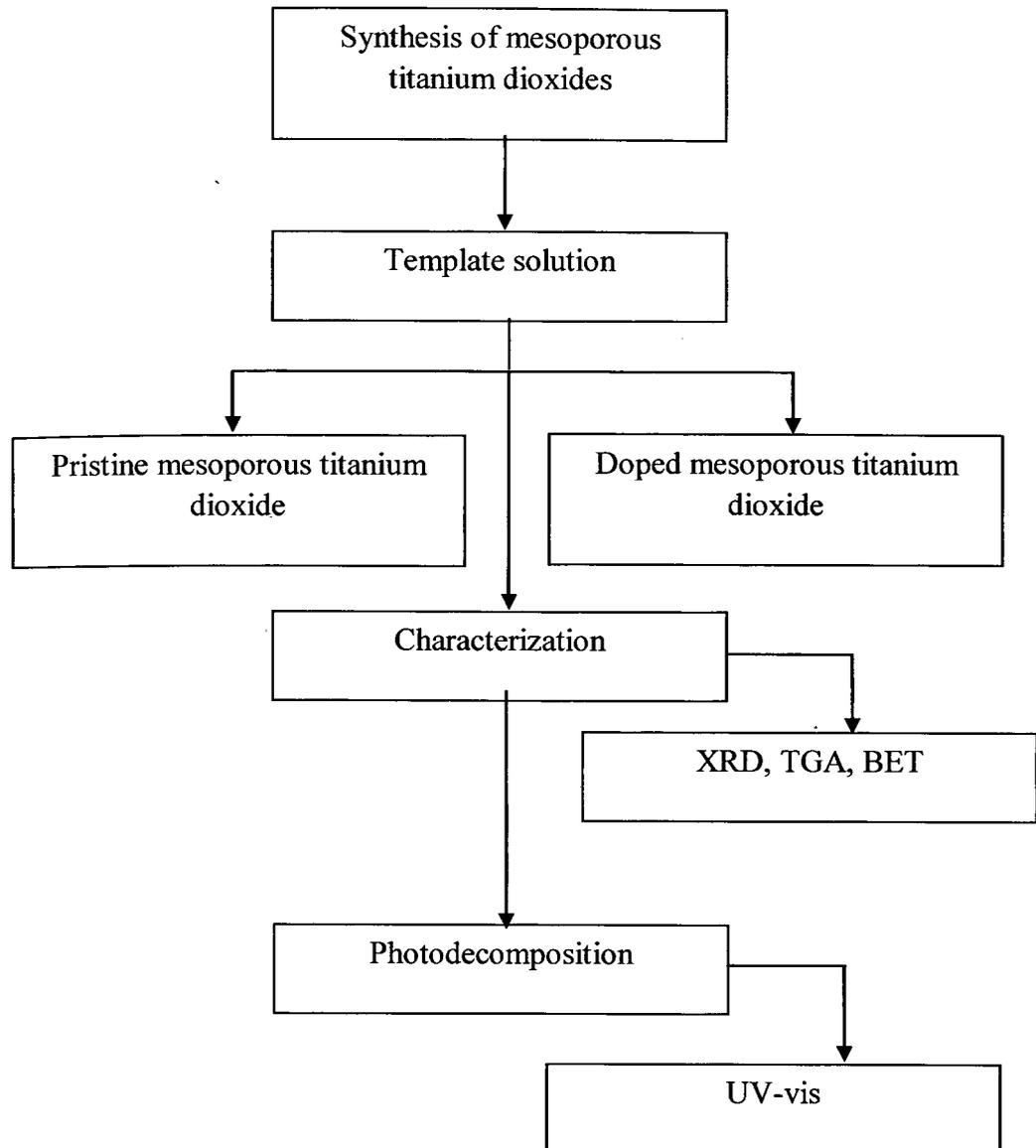
Figure 1.1: Flowchart of the Research Methodology

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO_2 (Zhan et al., 2006). Main uses of Titanium Dioxide are in pigments, anti microbial coating and oxygen sensors. In pigments, TiO_2 used to give whiteness and opacity to products such as paints and coatings, plastics, paper, inks, fibres and food and cosmetics. In anti microbial coating, the Titania in TiO_2 has photo catalytic property which makes the material a candidate for applications such as medical devices, food preparation surfaces, air conditioning filters, and sanitary ware surfaces. In oxygen sensors, titania can be used to sense the amount of oxygen present in an atmosphere which is used for studying atmosphere (Peng et al., 2005).

been investigated, and there have been many studies focusing on the mechanisms behind the primary processes of photocatalysis in order to prepare and design catalysts with high reactivity and efficiency. The small particle effect, size quantization effect, and high dispersion effect on photocatalysis were identified in the period 1980–1988, leading to the development of photofunctional zeolite catalysts that incorporated various transition metal cations, in their framework structures (Wang et al., 1999).

Then, in the 1990s, the focus of the investigations shifted to the use of TiO_2 photocatalysts in the decomposition of toxic compounds dissolved in water and air since TiO_2 exhibited a high photocatalytic reactivity for the degradation of organic compounds into CO_2 and H_2O even under weak UV light irradiation from sunlight. In 1995, the photo-induced superhydrophilicity of TiO_2 thin film photocatalysts was observed by Fujishima, resulting in the use of TiO_2 thin films in photofunctional materials having self-cleaning and antifogging properties (Tsujiko et al., 2000). Thus, not only powdered catalysts, but also thin film catalysts could be utilized in photofunctional materials in applications for creating and sustaining a cleaner and safer environment.

Through the years, we have seen a great evolution not only in catalytic and photocatalytic research, but also in various applications. TiO_2 catalysts are especially promising as some of the most stable, nontoxic, readily available and photofunctional materials known today. Since the development of visible light-sensitive second-generation TiO_2 photocatalysts using advanced ion-engineering techniques, such as metal ion-implantation and RF magnetron sputtering deposition, the challenge now is to engineer more highly efficient and effective TiO_2 photocatalysts that can operate under both UV and solar or visible, natural light (Hou et al., 2007).

2.3   Metal-doped Catalysts

The presence of the doping ions in the titanium dioxide structure caused significant absorption shift to the visible region compared to pure TiO_2 powder. Coupling TiO_2 with other metal oxides such as tungsten trioxide (WO_3) and Vanadium Pentoxide (V_2O_5) is an approach that has received much attention for improving the photocatalytic properties of titanium dioxide (Marci et al., 1996). The consequence of titanium dioxide modification by metal doping on the oxidation efficiency of cyclic hydrocarbons during irradiation over TiO_2 photocatalysts is investigated and the results evidenced the lower activities for both p- and n-type doped photocatalysts in comparison to pure titanium dioxide of similar texture. The lowest photocatalytic activity observed for chromium-doped TiO_2 was clarified as a consequence of chromium ions behavior as the recombination center for the photogenerated charge carriers and this suggestion was verified by photoconductivity experiments and lifetime of charge carriers measurements (Kown et al., 2000).

2.4   Sol-gel Synthesis

In this work, focus was on the preparation and investigation mesoporous titanium dioxides. For the synthesis, a sol-gel method was used. The advantages of the sol-gel technique are molecular scale mixing of the components, high purity of the precursor, and homogeneity of the sol-gel products with a high isotropy of physical, morphological, and chemical properties. The sol-gel technique is based on hydrolysis of liquid precursors and formation of colloidal sols (Rampaul et al., 2003). This method also may provide good control over stoichiometry and reduced sintering temperature. This is especially important if one of the components are volatile. May also enable production of low temperature phases (Hou et al., 2007).

2.5 Template Solution

In this research, template solution was prepared by dissolving hexadecyltrimethyl ammoniumbromide (CTAB) in isopropanol. Mesoporous materials prepared using molecular assemblies of surfactant as template have a highly surface area with tailored pore structure and have gathered increasing attention because of their possible application as adsorbent, catalyst, and separatory material (Ahn et al., 1999).
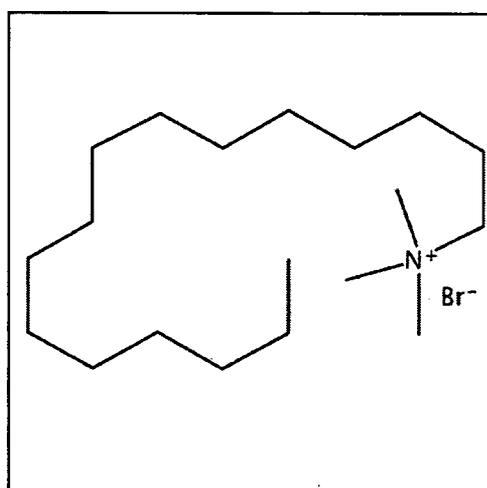
Figure 2.2: Hexadecyltrimethyl ammoniumbromide (CTAB) molecular structure

Source: Chemyq.com

2.6 Structure of Titanium Dioxide Surface

Titanium dioxide crystallizes in three major different structures which are rutile (tetragonal, D_{4h}^{14}-P42/mnm, a=b=4.584 Å, c=2.953 Å), anatase (tetragonal, D_{4h}^{19}-141/amd, a=b=3.782 Å, c=9.502 Å) and brookite (rhombohedrical, D_{2h}^{15}-Pbca, a=5.436 Å, b=9.166 Å, c=5.135 Å) (Dubrovisky et al., 2001). However, other structures exist as well, for example, cotunnite TiO_2 has been synthesized at high pressures and is one of the hardest polycrystalline materials known.

On the other hand, only rutile and anatase play any role in the applications of TiO_2 and are of any interest here as they have been studied with surface science techniques. Their unit cells are shown in Figure 2.3. The tetragonal bulk unit cell of rutile has the dimensions, a=b=4.587 Å, c=2.953 Å, and the one of anatase a=b=3.782 Å, c=9.502 Å. In both structures, slightly distorted octahedra are the basic building units. The bond lengths and angles of the octahedrally coordinated Ti atoms are indicated and the stacking of the octahedra in both structures is shown on the right side.

In both structures, the basic building block consists of a titanium atom surrounded by six oxygen atoms in a more or less distorted octahedral configuration. In each structure, the two bonds between the titanium and the oxygen atoms at the aspices of the octahedron are slightly longer. A sizable deviation from a 90° bond angle is observed in anatase. In rutile, neighboring octahedra share one corner along ⟨1 1 0⟩ — type directions, and are stacked with their long axis alternating by 90° (see Figure 2.3 as well as Figure 2.4) (Diebold et al., 2000).

In anatase the corner-sharing octahedra form (0 0 1) planes. They are connected with their edges with the plane of octahedra below. In all three TiO_2 structures, the stacking of the octahedra results in threefold coordinated oxygen atoms. The rutile (1 1 0) surface is the most stable crystal face and simple guidelines can be used to essentially predict the structure and the stability of TiO_2 (1 1 0)-(1×1) (Sambrano et al., 1997). Because these concepts are very useful for the other crystal faces of TiO_2 as well other oxide materials, they are exemplified for this surface. Although the TiO_2 (1 1 0) surface is very stable, it nevertheless reconstructs and restructures at high temperatures under both oxidizing and reducing conditions (Charlton et al., 2000).
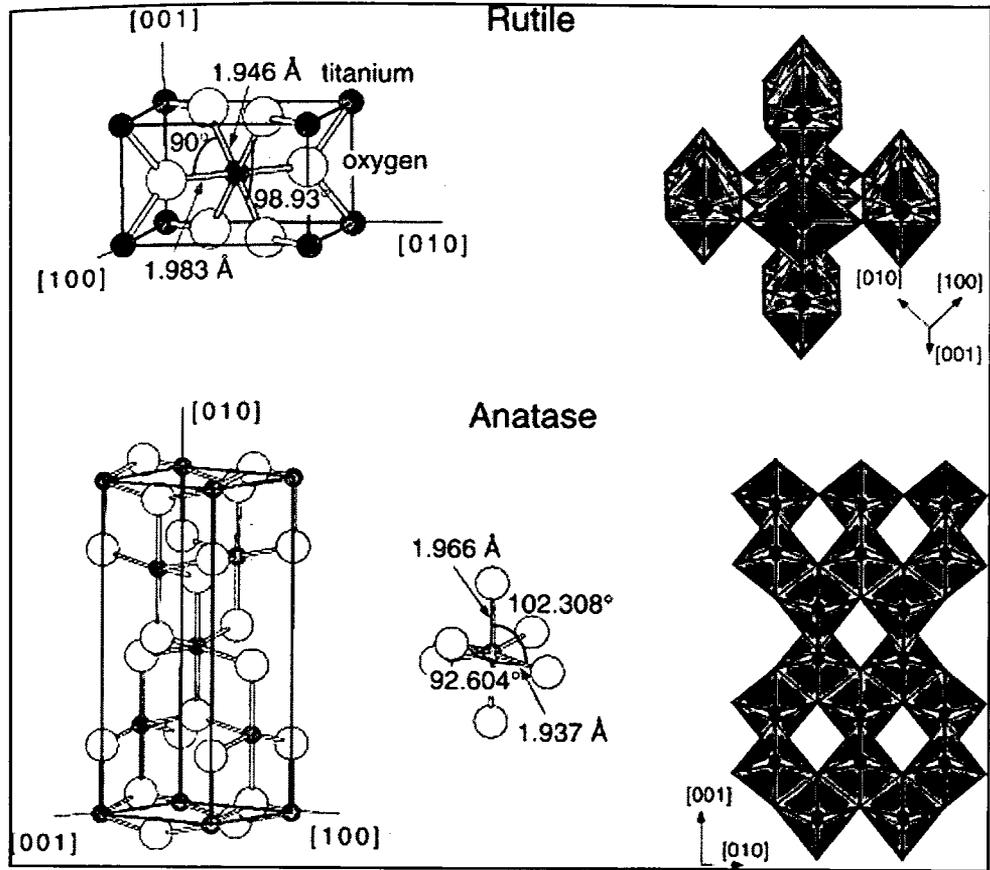
Figure 2.3: Bulk structures of rutile and anatase

Source: New Orleans 2002
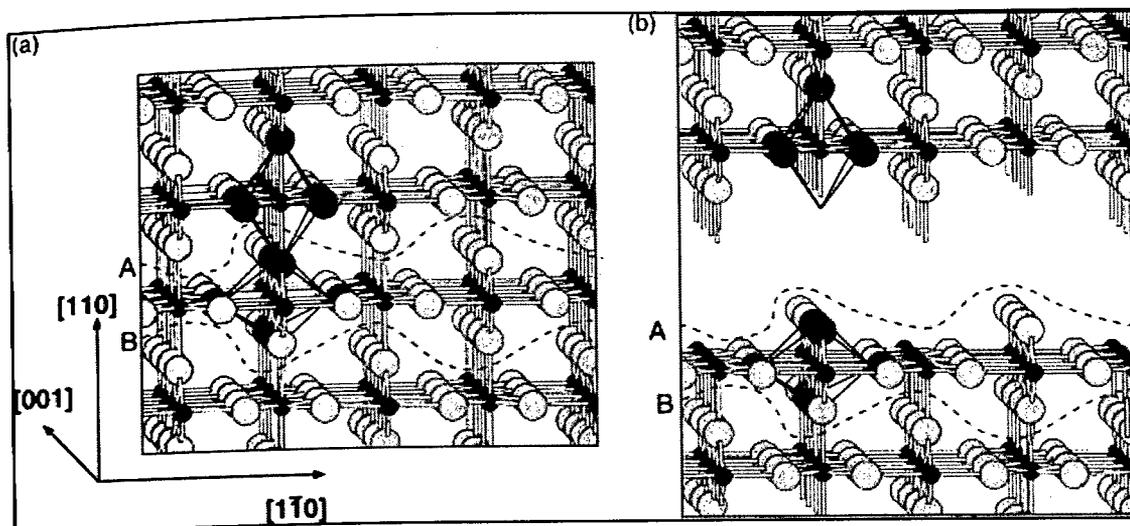
Figure 2.4: (a) Ball-and-stick model of the rutile crystal structure. It is composed of slightly distorted octahedra, two of which are indicated. Along the [1 1 0] direction these octahedra are stacked with their long axes alternating by 90°. Open channels are visible along the [0 0 1] direction. The dashed lines A and B enclose a charge-neutral repeat unit without a dipole moment perpendicular to the [1 1 0]-direction (a 'type 1' crystal plane according to the classification in (LaFemina et al., 1994)). (b) The crystal is 'cut' along line A. The same number of Ti→O and O→Ti bonds are broken, and the surface is autocompensated (Harrison et al., 1999). The resulting (1 1 0) surfaces are stable and overwhelming experimental evidence for such (1×1)-terminated TiO_2 (1 1 0) surfaces exists.

Source: New Orleans 2002