SOL-GEL DERIVED [illegible] ALLINE TITANIA CATALYSED PHOTODEGRADATION OF METHYLENE BLUE FROM AQUEOUS SOLUTION

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ABSTRACT

Titanium dioxide was widely used as photocatalyst for organic pollution degradation. Many researchers have reported that TiO_2 is one of the most active catalyst in pesticides, phenols and the degradation of dyes. In this study, silver doped TiO_2 nanoparticles (TiO_2-Ag) was succesfully prepared via sol-gel method and ultrasonic technique. For characterization of TiO_2-Ag, Thermal Gravimetric Analysis (TGA), X-Ray Diffaction (XRD) and Surface Area Analysis (BET) techniques were used. For the analysis of the photocatalytic reaction, TiO_2-Ag was undergo with the photodegradation of methylene blue (MB) dye in aqueous solutions and observed via UV-visible Spectroscopy. From the research, XRD showed the grain size of TiO_2-Ag was smaller than commercialize titanium dioxide. For BET, the surface area of TiO_2-Ag was higher than commercialize than titanium dioxide. On the other hand, characterization by using TGA showed that TiO_2/P-25 and TiO_2 doped with silver were thermodinamically stable. TiO_2 shows an intense absorption peak at 665 nm in UV and the intensity of this peak changes with concentration. The testing of the photocatalytic reaction of catalyst TiO_2 was examined using the methylene blue with presence and absence of H_2O_2. In this photocatalytic activity testing, the rate of the degradation MB were done and compared under various of conditions. This testing showed that the degradation of methylene blue was efficient by using TiO_2-Ag compared to P-25. It was observed, in presence of oxidizing agent (H_2O_2), the rate of degradation methylene blue increases significantly.

ABSTRAK

Titanium dioksida digunakan secara meluas sebagai fotokatalis degradasi pencemaran organik. Ramai penyelidik telah melaporkan bahawa TiO_2 merupakan salah satu pemangkin yang paling aktif dalam racun perosak, fenol dan degradasi pewarna. Dalam kajian ini, perak didopkan TiO_2 nanopartikel (TiO2-Ag) telah berjaya disediakan melalui kaedah sol-gel dan teknik ultrasonik. Untuk pencirian TiO_2-Ag, Analisis Gravimetrik Terma (TGA), X-Ray Diffaction (XRD) dan Analisis Luas Permukaan (BET) teknik digunakan. Untuk analisis tindak balas fotokatalik, TiO_2-Ag telah dijalankan dengan penyahwarnaan metilena pewarna biru (MB) dalam larutan akueus dan diuji melalui Spektroskopi cahaya nampak. Dari penyelidikan, XRD menunjukkan saiz bijian TiO_2-Ag adalah lebih kecil daripada komersial titanium dioksida. Untuk BET, luas permukaan TiO_2-Ag adalah lebih tinggi daripada komersial titanium dioksida. Sebaliknya, pencirian dengan menggunakan TGA menunjukkan bahawa TiO_2/P-25 dan TiO_2 yang didopkan dengan perak adalah termodinamik stabil. TiO_2 menunjukkan puncak penyerapan keamatan pada 665 nm UV dan keamatan ini berubah dengan kepekatan. Tindak balas fotokatalitik pemangkin TiO_2 telah diuji menggunakan metilena biru dengan kehadiran dan ketiadaan H_2O_2. Dalam ujian aktiviti fotokatalitik, kadar penyahwaranaan MB telah dilakukan dan dibandingkan di bawah pelbagai keadaan. Ujian ini menunjukkan bahawa degradasi metilena biru yang cekap adalah dengan menggunakan TiO_2-Ag berbanding P-25. Ia diperhatikan, dalam kehadiran agen pengoksidaan (H_2O_2), kadar biru metilena degradasi meningkat dengan ketara.

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A	Remaining absorbance
A_o	Absorbance of the primal
θ	Theta
k	Constant
λ	X-ray wavelength
β	Full width at half maximum of peak

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
MB	Methylene blue
min	minutes
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
UV	Ultraviolet
UV-vis	Ultraviolet Visible
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Titanium dioxide was lately received wide attention because it leads to non-toxic final products and showed high degradation efficiency. Besides, it is often included in many cosmetic preparations to reflect light away from the skin. It is also a major component of sun block to deter the absorption of ultraviolet (UV) rays from the sun, the concentration of which determines the product's Sun Protection Factor. Since titanium dioxide reflects light effectively, it is ideal for use as a protective coating for many products such as automobile parts and optical mirrors. It is also incorporated into paint. In fact, due to its refractive ability, it is a component of paints used to coat cars, boats, and airplanes.

In addition, titanium dioxide is found in a number of construction and building materials. The plastic industry also makes use of titanium dioxide as a coating to absorb UV light and render increased durability. Besides, TiO_2 electrode was used to degrade dyes and various environmental clean-up applications such as water purification, water treatment materials semiconductor in dye-sensitized solar cell, catalysts and gas sensors.

The study of these catalysts expand to all areas including synthesis, characterization of structures, and investigation potential applications. In the beginning, the research on catalysts was focused on the synthesis and characterization of titanium dioxide. For the synthesis of nanocrystalline titanium dioxide, one of the well-known methods to synthesis TiO_2 coatings was the sol-gel method (Samuneva et al., 1993).

In addition, characterization of nanocrystalline TiO_2 doped with silver was used BET, X-ray Diffraction (XRD), Thermal Gravimetric Analysis (TGA) and UV-vis Spectroscopy. Titanium dioxide or well known as titania is naturally occuring oxide of titanium. Titania exists in a number of crystalline forms and the most important of phase are anatase and rutile. There are various of industrial applications for this mineral and has a very high refraction properties.

1.2 Problem Statement

Most dyes and pigments are considered either inert or non-toxic, although some are not totally innocuous (Laing, 1991). Interest in the environmental behavior of dyes is prompted primarily by concern over their possible toxicity.and carcinogenicity, heightened by the fact that many dyes formerly were made of known carcinogens such as benzidine, which may be reformed as a result of metabolism (Clarke and Anliker, 1980).

Most dyestuffs are designed to be resistant to environmental conditions like light, effects of pH and microbial attack (Pagga and Taeger, 1994). Hence, their presence is unwarranted, and it is desirable to remove coloring material from effluents, before their discharge in the environment. The removal of such compounds at such low levels consists a difficult problem. Among the method, TiO_2 has been succesfully used to decolorized and mineralize many organic pollutants including several dye and their intermediates present in aqueous systems using both artificial light and under sunlight using solar technology (Muruganandham and Swaminathan, 2004).

Thus, this research was conducted to investigate the decolorization of methylene blue and kinetically to confirm the high activity of nanocrystalline TiO_2 doped with silver in the color-removal process.

1.3 Objectives of the Study

This research was conducted :

1. To synthesis the nanocrystalline TiO_2 doped with silver.

2. To characterized the physical properties of nanocrystalline TiO_2 doped with silver.
3. To determine the degradation of methylene blue through photocatalytic testing.

4. To study the effect of hydrogen peroxide as oxidation agent in degradation of methylene blue.

1.4 Scope of the Study

The scope of this study includes the synthesis of nanocrystalline TiO_2 doped with silver. The nanocrystalline TiO_2-Ag was succesfully synthesized by sol-gel method coupled with ultrasonic technique The photocatalytic testing of nanocrystalline TiO_2-Ag was investigated through the photodegradation of methylene blue in varied conditions.

The characterization of nanocrystalline TiO_2-Ag was using some instruments such as Surface Area Analysis (BET), X-ray Diffraction (XRD) and Thermal Gravimetric Analysis (TGA). The degradation of methylene blue was determined by observed the reducing concentration of methylene blue via UV-vis spectroscopy.

1.5 Outline of the Study

This dissertation illustrates the information concerning the synthesis, characterization and photocatalytic reaction of the nanocrystalline TiO_2 doped with silver by sol-gel process via ultrasonic irradiation. Chapter 1 elucidates the research background and the important strategies to respond the current issue. Chapter 2 presents the literature review regarding this project which contains some background information about the whole research done. Chapter 3 describes the research methodology with the characterization techniques used in this research as shown in the flowchart in Figure 1.1. Chapter 4 explains the results and discussions of the photodegradation of methylene blue from aqueous solution and its characterization. Finally, Chapter 5 was summarized the results obtained with recommendation for future work.

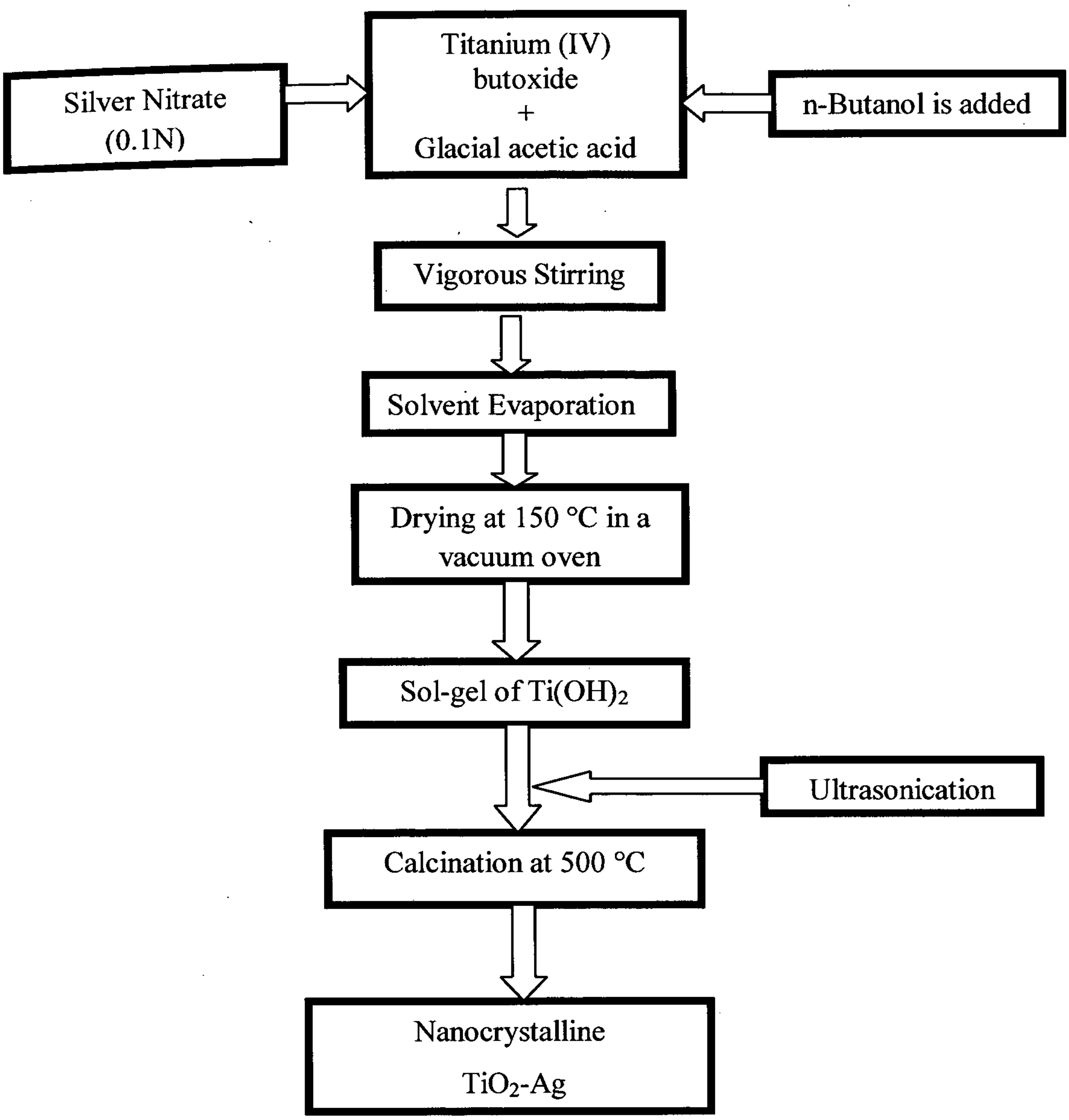

Figure 1.1 : Flowchart of the research methodology

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Industrial textile dyes are present in wastewaters at different concentrations. Dye pollutants in wastewaters are the principal source of environmental aqueous contamination. The textile mills is discharge the wastewater into the local environment without any treatment. Environmental contamination by these toxic chemicals is emerging as a serious global problem. Colored solutions containing dyes from effluents of textile, dyeing and printing industries may cause skin cancer due to photosensitization and photodynamic damage (Arora, Bhati, Punjabi and Sharm , 2010). Therefore, they need to be removed from wastewaters which are economical, ecofriendly and less time taking.

Previous research efforts have focused on various biological, chemical, and physical techniques for treating dyes. Biological treatment has been effective in reducing dyehouse effluents and when used properly has a lower operating cost than other. However, it has been also reported that most of the dyes are only adsorbed on the sludge and are not degraded (Pagga and Taeger, 1994).

Due to the above mentioned disadvantages, there is a active search for highly effective method to degrade the dyes into environmentally compatible products. Physical methods are also ineffective for the pollutants which are not readily adsorbable or volatile and have further disadvantages that they simply transfer the pollutants to another phase rather than destroying them. Due to the above mentioned disadvantages, there is a active search for highly effective method to degrade the dyes into environmentally compatible products. It has been revealed from the literature that photocatalysis can be used to destroy the dyes using semiconductor catalyst under light irradiation (Neppolian, Sakthivel, Palanichamy, Arabindoo and Muruganesan, 1998).

This chapter was focused on the catalysts that can degrade the dyestuff . Within the overall category of dye stuffs, methylene blue is one of the most important basic dye. More specifically, the efficiency of the photocatalysts was explored and effective methods for degrading these types of compounds were described.

2.2 Photodegradation

Photodegradation is a process of decomposition of the material upon exposure to radiant energy such as the action of light. Most of the investigations were carried out under UV light because TiO_2 absorbs light of wavelength 400 nm or shorter. Photocatalytic degradation of organic contaminants using solar radiation is highly economical compared with the processes using artificial UV radiation. In order to utilize sunlight or rays from artificial sources more effectively in photocatalytic reactions, photocatalysts with strong absorptions in the visible region should be developed. For this purpose, doping of TiO_2 powder with transition metals has been investigated (Ohno, et al., 1999 ; Yin et al., 2005).

The degradation of methylene blue was calculated by Equation 2.1 :

$$\text{Degradation} = \frac{Ao - A}{Ao} \qquad (2.1)$$

Photocatalytic degradation of methylene blue in the aqueous suspensions of anatase TiO_2/P-25 nanopowder and silver deposited TiO_2 nanoparticles with UV light was investigated. The enhancement of photocatalytic activity of silver doped TiO_2 is found to be due to the following mechanism in Figure 2.1.

Silver nanoparticles was deposited on TiO_2 act as electron traps, enhancing the electron–hole separation and the subsequent transfer of the trapped electron to the adsorbed O_2 acting as an electron acceptor.

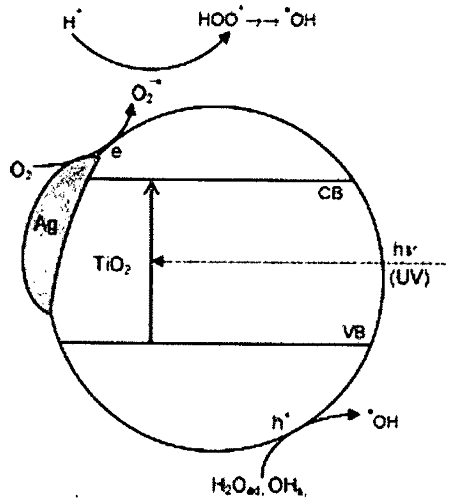

Figure 2.1 : TiO_2 photosensitisation pathway under UV irradiation.

Source : Sobana et. al

2.3 Metal Doped

In many cases significantly decreased activity has been described as resulting from doping (Yin et al., 2005). The selection of a suitable metal dopant is thus challenging.

The initiation step of the photocatalytic process consists in the generation of electron-hole pairs upon irradiation of the material with a photon having energy at least equal to that of the bandgap of the photocatalyst. The electron-hole pairs formed can either recombine in the bulk or travel up to the surface, where they can participate in chemical reaction involving species adsorbed on the external titanol groups. As a consequence, only UV light is able to create electron-hole pairs and to initiate the photocatalytic processes. Therefore, evident that any modification of the TiO_2-based photocatalysts, resulting in a lowering of its bandgap (Isono, Yoshimura and Esumi, 2005), is representing a breakthrough in the field. This is the reason why so many scientific works have appeared during recent years to enhanced photoactivity in the visible. Metal doping is the best preparation which is doping TiO_2 with various transitions metals such as Au, Ag, Pt, Cr, Nb, V, Mn, and Fe (Rodrigues et al., 2005 ; Kapoor, Uma, Rodriguez and Klabunde, 2005).

In this study, TiO_2 doped with silver metal was focused. Electrons in the valence band of TiO_2 are excited to the conduction band with formation of holes in the valence band. At the same time electrons of silver nanoparticles, when irradiated with the light their plasmon resonance wavelength are excited and transformed to adsorbed oxygen with formation of O^{2-}. The Ag nanoparticles are consequently oxidized by O^{2-} to colorless Ag^+ ions (Naoi, Ohko and Tatsuma, 2004 ; Chen, Zhang and Fang et al., 2004). In presence of TiO_2 these Ag^+ ions are reduced by the excited electrons and Ag nanoparticles are reformed. A limiting factor of the photocatalytic reaction is, therefore, recombination of the electron and hole prior to the superoxide activation step (Gerischer and Heller, 1991). Silver has been shown to have a beneficial influence on the photoactivity of nanocrystalline semiconductor (Chen and Nickel, 1996 ; Gouvêa et al., 2000 ; Height et al., 2006 ;). The combination of semiconductor substrate and metal cluster has been reported to give improved photocatalytic activity by trapping the photoinduced charge carriers, thereby improving the charge transfer processes (Abe et al., 1999 ; Subramaniam, Wolf and Kamat, 2001 ; Teoh et al., 2005).

The average grain size or crystal size of each anatase in these two kinds of titania powders was measured from analysis of the XRD diffraction line broadening using the Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{2.2}$$

In this equation, k is a constant equal to 0.89, λ, the X-ray wavelength equal to 0.154 nm, β,the full width at half maximum and θ, the half diffraction angle (Wu, 2004).

As well known, silver ions and silver shows good antibacterial activity (Takashi and Toshio, 1999). The silver ion was also the effective composition of most inorganic antibacterial agents. It is rational that introduction of silver ions into TiO_2 could improve antibacterial ability of TiO_2. Therefore, it is very important to study the influence of the silver dopant on the photoactivity of TiO_2 nanoparticles. In addition, this method could provide, in principle, a better homogeneity of iron on the surface and inside the particles.

2.4 TiO_2 Nanoparticles

Nanoparticles, which refers to particles with diameters smaller than 100 nm and materials with at least one dimension in the manometer scale. Nanoparticles induced much interest in researches because of their higher specific surface areas, quantum effects, and better quality in decomposing organic or inorganic materials in gaseous or liquid phase. As a result, synthesizing for nanoparticle TiO_2 has drawn much attention because of its electrochemical, optical, dielectric and electroconductive properties.

The synthesis of titanium dioxide has become a potential aspect in the field of inorganic materials preparation.The efficiency of titania is influenced by many factors such as crystallinity of the anatase phase (Nishimoto, Ohtani, Hajiwara and Kagiya, 1985), particle size, surface area (Zhang, Penn, Hamers and Banfield, 1994 ; Zhang, Wang, Zakaria and Ying, 1998), and the method of preparation (Reddy, Reddy and Manorama, 2001). It is known that the transformation behavior from the amorphous to the anatase or rutile phase is influenced by the preparation conditions (Kumar, Badrinarayanan, and Sastry, 2000).

A number of techniques, such as spray pyrolysis (Abou-Helal and Seeber, 2002), sol-gel method (Yu, Zhao, and Zhao, 2001), sputtering (Dumitriu et al., 2000 ; Zheng et al., 2001), solvothermal method (Lee, Kang, Cho et al., 2001), pulsed laser deposition (Paily, DasGupta, DasGupta et al., 2002), atomic layer deposition (Aarik, Aidla and Uustare et al., 2002), chemical vapour deposition (CVD) (Byun et al., 2000 ; Hitchman et al., 2002) and photoassisted CVD (Kaliwoh, Zhang and Boyd, 2002) were used to prepare new samples of silver-doped titania. Each of the techniques for the TiO_2 thin film preparation has its own advantages and disadvantages, and it remains unclear at present as to which of these will eventually prove to be the most cost or quality effective. One of the well-known methods to synthesize TiO_2 coatings is the sol-gel method (Samuneva, Kozhukharon and

Trapalis et al., 1993). By using this method, the uniform coatings can be synthesized on very large surfaces of substrates. Therefore, templates may be inducted into the sol-gel technology to control the crystalline structure and porous microstructure (Devi and Hyodo et al., 2002).

2.4.1 Synthesis of Titanium Dioxide

There have been many approaches to synthesize nanoparticles. In general, the methods to synthesize nanosized TiO_2 can be differentiated into two main categories which are one is based on liquid phase, and one is based on gaseous phase. Table 2.1 summarized the different synthesis method of titanium dioxide.

Table 2.1 : Different synthesis method of titanium dioxide.

Synthesis Method	Precursors	Reactant	Characterization	Literatu
Precipitation	$TiCl_3$		XRD, TGA, SEM, BET	Pedraza and Vazquez, 1999
	$TiCl_2$		XRD, AFM, TEM, PSD	Xie and Yuan, 20C
Solvothermal	Tetratitanate	H_2O	TG-DTA, TEM, UV-Vis, GC	Yin, 2003
	TTIP		XRD, TEM, BET	Kim et al. 2003
	TTIP	$CHCl_3$	XRD, SEM, DLS, UV-Vis	Lee et al., 2001
Hydrothermal microemulsio n	$TiOCl_2$	Methylene blue	XRD, TEM, BET, UV-Vis	Lu and Wen, 200
Microemulsio n	Tetrabutyl titanate		TEM, FE-SEM	Tang et al 2007
	Tetrabutyl titanate	Methyl orange	TEM, XRD, FTIR	Pu et al., 2007

Table 2.1 : Continued

Synthesis Method	Precursors	Reactant	Characterization	Literatur
Combustion synthesis	$TiCl_4$		XRD, XPS, TEM, BET, FTIR	Zhao et al. 2008
	Titanyl nitrate	Cu^{2+} , Cr^{6+}	XRD, TEM, BET, TG-DTA, XPS, IR and UV spectroscopy	Aarthi and Madras, 2008
	TTIP		TEM, XRD, SMPS	McCormi , 2006
Sol-gel	$TiCl_4$		XRD, TEM, DLS	Matijevic al., 1977
	TTIP	Malachite green (MG), Benzamide (BZ), 4-hydroxy-benzoic acid (4-HBZ)	XRD, BET	Bessekhou d et al., 2003
	1. TTIP 2. Titanium butoxide	Organic carbon (OC)	XRD, TEM, BET, FTIR, TGA, TOC	Watson et al., 2003
	1.Tetraethylorthotitanate 2. Tetraisopropyl orthotitanate (TTIP) 3. Tetrabutylorthotitanate		XRD, TGA, BET, TEM	Crisan et al., 2007
	TTIP		TG-DTA, TEM, XRD, Raman	So et al., 2001
	Tetrabutylorthotitanate		XRD, TEM	Juengsuw tananon et al., 2007
Sol-gel	Tetrabutyl titanate		XRD, TEM, UV-Vis, DSC/TGA	Li et al., 2004
	Tetrabutyl orthotitanate	Methyl orange	TG-DTA, XPS, XRD, SEM, TEM, UV-Vis	Yu et al., 2001
CVD	Titanium (IV) n-butoxide		SEM, TEM, XRD, TG-S, DTA, BET	Ahonen et al., 2001