Study of the Bandgap of Synthesized Titanium Dioxide Nanoparticules Using the Sol-Gel Method and a Hydrothermal Treatment

Sergio Valencia, Juan Miguel Marín and Gloria Restrepo*

Applied Physical Chemistry Processes, University of Antioquia, Medellin, Colombia

Abstract: In this work optical properties of titanium dioxide nanoparticles were studied. Titanium dioxide nanoparticles were synthesized by the sol-gel method followed by a hydrothermal treatment using tetraisopropyl orthotitanate (TIOT) and 2-propanol. The synthesized samples were characterized by X-ray diffraction (XRD), UV-Vis diffuse reflectance spectroscopy (UV/DRS) and nitrogen adsorption-desorption methods. The bandgap energy was obtained using the Kubelka-Munk reemission function. The catalyst synthesized with a molar ratio of $R_{1\ (water/TIOT)} = 3.5$ and $R_{2\ (2\text{-}propanol/TIOT)} = 15$ has a predominately anatase phase. It also has a high photo degradation of methyl orange compared to TiO_2 Degussa P-25. A shift band gap energy of 3.27 was observed.

Keywords: Titanium dioxide, hydrothermal treatment, sol-gel method, band gap.

1. INTRODUCTION

Titanium oxide (TiO_2) is a material with wide application due to its optical and electronic properties. It is used as an ingredient in sunscreen lotions and food products, as a pigment in paints and as semiconductors in the photocatalytic degradation of organic compounds [1]. In TiO_2, the crystalline phase, the composition and the surface states strongly affect the electronic structure and the charge properties [2]. The photocatalytic activity of TiO_2 depends on its present phase. There are three crystalline forms of TiO_2: anatase, rutile and brookite. Anatase phase is metastable and has the greater photocatalytic activity; rutile has a high chemical stability but is less active [3,4]. Besides, some TiO_2 with a large quantity of anatase and a small quantity of rutile exhibits a higher photocatalitic activity than in the pure anatase or rutile phases [2,5]. The absorption spectrum of a semiconductor defines its possible uses. The useful semiconductors for photocatalysis have a bandgap comparable to the energy of the photons of visible or ultraviolet light, having a value of $E_g < 3.5$ eV. The majority of authors have determined that in TiO_2 the rutile has a direct band gap of 3.06 eV and an indirect one of 3.10 eV and the anatase has only an indirect band gap of 3.23 eV [6,7]. However, Reddy's work [1] shows that a bandgap of anatase phase from the plot for indirect transition are quite low (2.95 – 2.98 eV), which led them, contrary to the other authors, to conclude that the direct transition is more favorable for TiO_2 nanoparticles with anatase phase. There have been reported values in the literature from 2.86 to 3.34 eV for the anatase phase, the differences being attributed to variations in the stoichiometric of the synthesis, the impurities content, the crystalline size and the type of electronic transition [8,9]. In this work the optical properties are evaluated in context of the bandgap of the synthesized TiO_2 samples with the sol-gel method and the hydrothermal treatment, using a crystallization temperature of 200ºC for 2 hours, and TIOT as precursor [8,10-14]. The bandgap was calculated by means of the reflectance diffusion technique, which shows an abrupt increase in the absorbance of the longitude or the wave corresponding to the energy of the prohibited band.

*Address correspondence to this author at the Applied Physical Chemistry Processes, University of Antioquia, Medellin, Colombia; Tel: 57 4 2196578; Fax: 57 4 2196543; E-mail: gloma@udea.edu.co

2. MATERIALS AND METHODS

2.1. Reactives

Teraisopropyl orthotitanate (TIOT), 2-propanol and hydrochloric acid are from Merck, methyl orange from Carlo Erba, titanium dioxide P-25 Degussa and Milli-q water.

2.2. Preparation of the Samples

The titanium precursor TIOT and water were added dropwise into the 2-propanol solvent, continuously stirring for 2 hours, after that 3 drops of HCl 3M was added. For the crystallization under autogenous pressure the solution obtained was put in a steel-teflon reactor and heated to 200ºC for 2 hours, after which the sample was filtered and washed with 30 mL of 2-propanol and was dried at 100ºC for 1 hour. In order to study the effect of some variables on the synthesis of TiO_2 a 3^2 factorial design was used, with $R_{1\ (water/TIOT)}$ and $R_{2\ (water/TIOT)}$ as factors with the levels 2.85, 3.5, 60 and 10, 15, 20, respectively (Table **1**).

2.3. Characterization

XRD analysis was performed using an x-ray diffractometer (Rigaku Miniflex) with Cu-Kα radiation in 2θ range from 10º to 60º; the reflectance diffusion spectrum UV-Vis (UV/DRS) was obtained using a UV-Vis Evolution 600 spectrometer, a thermo Electron Corporation with a reflectance diffuse accessory; the superficial area of Brunauer-Emmett-Teller was determined using a Gemini V Miromerities.

2.4. Photocatalytic Activity Measurements

In order to evaluate the photocatalytic activity of each of the synthesized TiO_2, 37.5 mg of TiO_2 was added in 250 mL

1874-088X/10 2010 Bentham Open

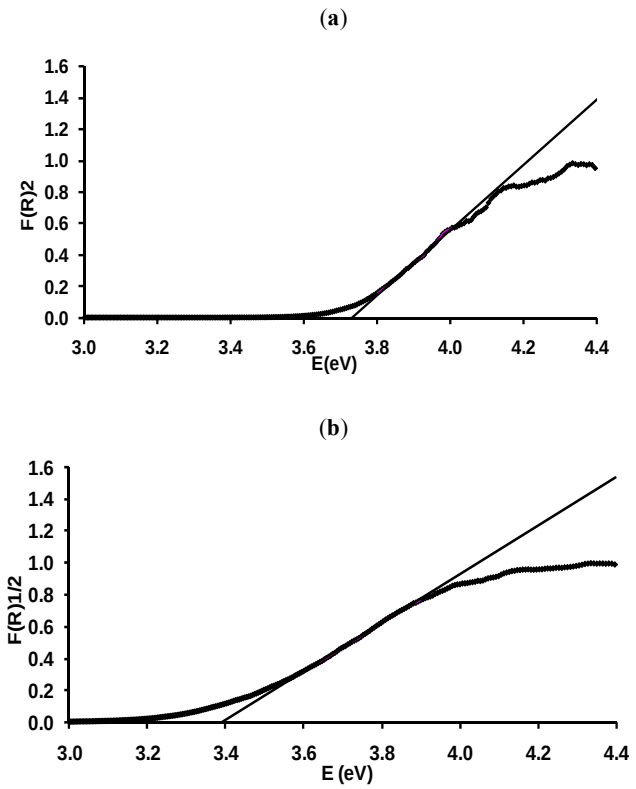

Fig. (5). Absorbance spectra for amorphous TiO_2 samples at $R_{1(water/TIOT)}$ = 0.17: **a**) direct electronic transition type and **b**) Indirect transition type.

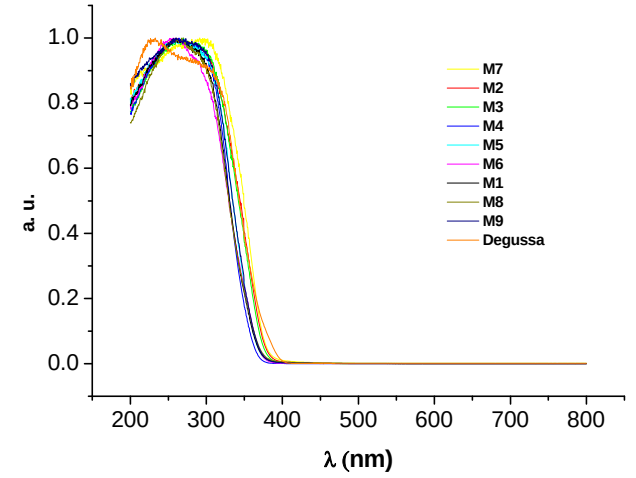

Fig. (6). Diffusion reflectance spectrums of the synthesized TiO_2 samples.

of over 159.48 to 226.26 $m^2 \cdot g^{-1}$. These materials show an indirect type band gap close to those reported in the bibliography of 3.23 eV for the anatase phase. Besides, found optical absorption shows that the direct bandgap verses indirect bandgap permits the determination of the crystillinity of a material; for an amorphous material the band gap is greater than 3.4 eV independent of the transition types. All the properties of the synthesized materials

Table 2. Direct and Indirect Bandgap Transitions for Synthesized TiO_2 Samples

Sample	Bandgap (eV)	
	Direct	Indirect
M1	3.40	3.15
M2	3.43	3.13
M3	3.47	3.18
M4	3.63	3.25
M5	3.58	3.24
M6	3.60	3.27
M7	3.62	3.22
M8	3.63	3.19
M9	3.58	3.14

Table 3. Superficial Area of TiO_2 Samples Synthesized the Sol-Gel Method and the Hydrothermal Treatment

Muestra	S_{BET} ($m^2.g^{-1}$)
M1	159.48
M2	162.30
M3	169.11
M4	175.09
M5	177.65
M6	179.11
M7	203.33
M8	219.86
M9	226.26
Degussa	48.90

Table 4. Photocatalytic Degradation of a Methyl Orange Solution (20ppm) with the Synthesized TiO_2 Samples (150 pm of TiO_2), Adsorption Time 1 Hour, Degradation 7 Hours

Sample	% Degradation
M1	60.86
M2	62.43
M3	60.69
M4	79.89
M5	100.0
M6	81.11
M7	75.16
M8	61.55
M9	58.83
Degussa	100.0

depended on the $R_{1(water/TIOT)}$ molar ratio where the catalyst with the greater photocatalytic activity has the molar ratios: $R_{1(water/TIOT)}$=3.5 and $R_{2(2\text{-propanol/TIOT})}$= 15.

ACKNOWLEDGEMENT

The authors wish to thank the financial support to the University of Antioquia through the "Estrategia de Sostenibilidad de Grupos 2009-2010" program.

REFERENCES

[1] Reddy K, Manorama S, Redd A. Bandgap studies on anatase titanium dioxide nanoparticles. Mater Chem Phys 2002; 78: 239-45.

[2] Jing l, Li S, Song S, Xue L, Fu H. Investigation on the electron transfer between anatase and rutile in nano-sized TiO_2 by means of surface photovoltage technique and its effects on the photocatalytic activity. Solar Energy Mater Solar Cells 2008; 92: 1030-6.

[3] Wang G. Hydrothermal synthesis and photocatalytic activity of nanocrystalline TiO_2 powders in ethanol-water mixed solutions. J Mol Catal A: Chem 2007; 274: 185-91.

[4] Sahni S, Reddy B, Murty B. Influence parameters on the synthesis of nano-titania by sol-gel route. Mater Sci Eng A 2007; 452-453: 758-62.

[5] Francisco M. y Mastelaro V. Inhibition of the anatase-rutile phase transformation with addition of CeO_2 to CuO-TiO_2 system: Raman spectroscopy, X-ray diffraction, and textural studies. Chem Mater 2002; 14 (6): 2514-8.

[6] Welte A, Waldauf C, Brabec C, Wellmann P. Application of optical for the investigation of electronic and structural properties of sol-gel processed TiO_2 films. Thin Solid Films 2008; 516: 7256-9.

[7] Monllor-Satoca D, Gomez R, González-Hidalgo M, Salvador P. The "Diret-Indirect" model: An Alternative kinetic approach in heterogeneous photocatalysis based on the degree of interaction of dissolved pollutant species with the semiconductor surface. Catal Today 2007; 129: 247-55.

[8] Hidalgo M, Aguilar M, Maicu M, Navio J, Colon G. Hydrothermal preparation of highly photoactive TiO_2 nanoparticles. Catal Today 2007; 129: 50-8.

[9] Hossain F, Sheppard L, Nowotny J, Murch G. Optical properties of anatasa and rutile titanium dioxide: Ab initio calculations for pure and anion-doped material. J Phys Chem Solids 2008; 69: 1820-8.

[10] Marín JM, Restrepo G, Rios LA, Navío JA. Nueva ruta de síntesis para el dióxido de titanio. Rev Colomb Fís 2005; 37: 78-81.

[11] Su C, Tseng C, Chen L, You B, Hsu B, Chen S. Sol hydrothermal and photocatalysis of titanium dioxide. Thin Solid Films 2006; 498: 259-65.

[12] Wen B, Liu C, Liu Y. optimization of the preparation methods synthesis of meso structures TiO_2 with high photocatalytic activities. J Photochem Photobiol A: Chem 2005; 173: 7-12.

[13] Yu J, Wang G, Cheng B, Zhou M. Effects of hydrothermal temperature and time on the photocatalytic activity and microstructures of bimodal mesoporous TiO_2 powders. Appl Catal B: Environ 2007; 69: 171-80.

[14] Zhu J, Yang J, Bian Z, *et al*. Nanocrystaline anatase TiO_2 photocatalysis prepared *via* a facile low temperature nonhydrolitic sol-gel reaction of $TiCl_4$ and benzyl alcohol. Appl Catal B: Environ 2007; 76: 82-91.

[15] Liu G, Jin Z, Wang T, Liu Z. Anatase TiO_2 porous thin films prepared by sol-gel method using CTAB surfactant. J Sol-Gel Tech 2007; 41: 49-55.

[16] Yu H, Wang S. effects of water content and pH on gel-derived TiO_2-SiO_2. J Non-Crystal Solids 2000; 261: 260-7.

[17] Essick J, Mather R. Characterization of a bulk semiconductor's band gap *via* near-absorption edge optical transmission experiment. Am J Phys 1993; 61: 646-9.

[18] Willardson R, Beer A. Optical Properties of III-V Compounds. Academic Press New York 1967; pp. 318-400.

[19] Dressel M, Gruner G. Electrodynamics of Solids Optical Properties of Electron in Matter. Cambridge University Press 2002; pp. 159-65.

[20] Kottim G. Reflectance spectroscopy. Springer Verlag. New York 1969.

[21] Tandon S, Gupta J. Measurement of forbidden energy gap of semiconductors by diffuse reflectance technique. Phys Stat Sol 1970; 38: 363-7.

[22] Wendlandt W, Hecht H. Reflectance Spectroscopy. Wiley Interscience New York 1966.

[23] Sreen K, Poulose C, Unni B. Colored cool colorants based on rare earth metal ions. Solar Energy Mater Solar Cells 2008; 92: 1462-7.

[24] Bagheri-Mohagheghi M, Shahtahmasebi N, Alinejad M. The effect of the post-annealing temperature on the nano-structure and energy band gap of SnO_2 semiconducting oxide nano-particles synthesized by polymerizing-complexing Sol-gel method. Phys B: Condensed Matter 2008; 403: 2431-7.

[25] Ting C, Chen S. Structural evolution and optical properties of TiO_2 thin films prepared by thermal oxidation of sputtered Ti films. J Appl Phys 2000; 88: 4628-33.

[26] López S, Castillo S, Chávez J, Díaz K. Síntesis y caracterización óptica, eléctrica y estructural de películas delgadas de CS_2 depositadas por el método PECVD. Materia 2003; 8: 341-9.

[27] Oliva F, Avalle L, Santos E, Camara O. Photoelectrochemical characterization of nanocrystalline TiO_2 films on titanium substrates. J Photochem Photobiol A: Chem 2002; 146: 175-88.

[28] Litter M. Heterogeneous photocatalysis transition metal ions in photocatalytic systems. Appl Catal B: Environ 1999; 23: 89-114.

[29] Venkatachalam N, Palanichamy M, Murugesan V. Sol-gel preparation and characterization of nanosize TiO_2: Its photocatalytic performance. Mater Chem Phys 2007; 104: 457-9.

[30] Kolen'ko Y, Churagulov B, Kunst M, Mazerolles L, Colbeau Justin. Photocatalytic properties of titania powders prepared by hydrothermal method. Appl Catal B: Environ 2004; 54: 51-8.

[31] Kominami G, Kato J, Takada Y, *et al*. Novel synthesis of microcrystalline titanium(IV) oxide having high thermal stability and ultra-high photocatalytic activity: thermal decomposition of titanium(IV) alkoxide in organic solvents. Catal Lett 1997; 46: 235-40.

Received: October 14, 2009 Revised: October 16, 2009 Accepted: October 30, 2009