UNIVERSITI PUTRA MALAYSIA

PHOTOLUMINESCENT PROPERTIES OF TIO2 NANOSTRUCUTRES PREPARED BY HYDROTHERMAL METHOD

GOLNOUSH ZAMIRI

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By

GOLNOUSH ZAMIRI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for the Degree of Master of Science**

December 2013

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This thesis dedicates to

My father (Ali Zamiri), my mother (Kobra Fazeli),

my dear brothers (Reza and Roozbeh Zamiri) and my sister (Golriz Zamiri).

Abstract of thesis presented to the Senate of Universiti Putra Malaysia, in fulfillment
of the requirement for the degree of Master of Science

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GOLNOUSH ZAMIRI

December 2013

Chairman : Professor Azmi Zakaria, PhD

Faculty : Science

The major problem facing in the fabrication of TiO_2 nanostructure is about the control of its size and shape which have directly effect on its physical properties. The nanostructures prepared by hydrothermal method shows better structural, morphological and photocatalytic property. In the present study the fabrication of nanosize TiO_2 prepared by hydrothermal technique using Ethylenediamine (EN) and Thiourea (TH) as solvent has been investigated. The objectives of the work is to present a systematic study on the growth and characterization of TiO_2 nanostructures prepared by this method, and secondly, to experimentally study the effect of Mn doping on structural and photoluminescence properties of TiO_2 nanostructures. In this hydrothermal method, TiO_2 of micron size, EN and TH were dissolved in distilled water and then transferred to a teflon-lined autoclave. The precipitate was collected, washed with ethanol:water solution and then dried in an oven. The effect of temperature, time, precursors on structure and morphology of the TiO_2 were studied. To see the effect of Mn on TiO_2nanostructures, Mn, TiO_2, EN and TH were dissolved in distilled water and then transferred to an autoclave. The obtained powders were characterized by FTIR and photoluminescence (PL) spectroscopies, XRD, EDX, SEM, and VSM. Characterization by SEM confirmed that the samples are well crystalline nanostructure. The XRD patterns of all the products have diffraction peaks which well agree with those of a standard anatase TiO_2 (JCPDS No.21-1272). The SEM results show that the morphology of TiO_2 using EN and TH changed when the sample prepared at various hydrothermal temperatures, times and precursors. The PL study shows that the band gap energy of the TiO_2 nanomaterial increased to 3.23 eV compared to that of bulk state (3.20 eV). When doped with Mn, the XRD result confirmed that Mn goes into TiO_2 crystal lattice and the crystallite size decreases. The SEM images show that the morphology of some pure TiO_2 nanostructure was changed from nanorod and nanoparticle to flower-like after doping. The optical band-gap energy of the sample increases due to the decrease of material size and it behaved as a soft ferromagnet.

Tesis abstrak dikemukan kepada Senat Universiti Putra Malaysia, untuk memenuhi keperluan ijazah Master Sains

CIRI-CIRI KEFOTOPENDARCAHAYAAN STRUKTUR-NANO TIO2 DISEDIAKAN MELALUI KAEDAH HIDROTERMA

Oleh

GOLNOUSH ZAMIRI

Disember 2013

Pengerusi : Profesor Dr. Azmi Zakaria, Ph.D

Fakulti : Sains

Masaalah utama dihadapi dalam fabrikasi strukturnano TiO_2 adalah berkaitan dengan pengawalan saiz dan bentuknya yang mana secara terusnya terkesan keatas sifat fizikalnya. Strukturnano disediakan secara kaedah hidrotherma menunjukkan sifat struktur, morfologi dan ciri fotokatalitik yang lebih baik. Dalam kajian ini fabrikasi saiznano TiO_2 disediakan secara teknik hidroterma manggunakan Ethylenediamine (EN) dan Thiourea (TH) sebagai pelarut telah diselidiki. Objektif kajian adalah untuk mempersembahkan kajian sistematik pembesaran dan pencirian strukturnano TiO_2 disediakan dari kaedah ini, dan keduanya, untuk mengkaji kesan pendopaan Mn keatas struktur dan sifat-sifat strukturnano TiO_2. Dalam kaedah hidroterma ini, TiO_2 bersaiz micron, EN dan TH telah dilarutkan dalam air suling dan kemudian dipindahkan ke autoklev tersalut-teflon. Mendakan dikumpul, dibasuh dengan larutan etanol:air dan kemudian dikeringkan dalam oven. Kesan suhu, masa, prekerser keatas struktur dan morfologi TiO_2 telah dikaji. Untuk melihat kesan Mn keatas strukturnano TiO_2, Mn, TiO_2, EN dan TH dilarutkan dalam air suling dan kemudian dipindahkan kedalam autoklev. Serbok diperolehi telah dicirikan dengan XRD, EDX, SEM, VSM, dan spektroskopi-spektroskopi FTIR, kefotopendarcahayaan (PL). Pencirian oleh SEM mengesahkan bahawa sampel-sampel adalah nanostruktur hablor sempurna. Corak XRD dari semua produk mempunyai puncak-puncak pembelauan yang mana bersetuju benar dengan yang dari TiO_2 anates piawai (JCPDS No.21-1272). Hasil-hasil SEM menunjukkan bahawa morfologi TiO_2 menggunakan EN dan TH telah bertukar apabila sampel disediakan dibeberapa suhu, masa hidroterma dan perkerser. Kajian PL menunjukkan tenaga jurang jalur nanomaterial TiO_2 telah bertambah ke 3.24 eV berbanding dengan yang dari keadaan pukal (3.20 eV). Apabila didop dengan Mn, hasil XRD mengesahkan bahawa Mn masuk ke kekisi hablor TiO_2 dan mengecilkan saiz hablor. Imej-imej SEM menunjukkan bahawa sebahagian morfologi strukturnano TiO_2 tulin telah berubah daripada nano-batang dan nano-zarah ke bentuk-bunga selepas pendopan. Tenaga jurang jalur sampel bertambah disebabkan oleh saiz bahan dan ianya bersifat sebagai ferromagnet lembut.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
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LIST OF ABBREVIATIONS/SYMBOLS

TiO_2	Titanium Dioxide
EN	Ethylenediamine
TH	Thiourea
UV	Ultraviolet
DSCs	Dye-sensitized Solar Cells
1-D	1-Diamentional
XRD	X-ray Diffraction
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
PL	Photoluminescence
VSM	Vibrating Sample Magnetometer
CVD	Chemical Vapor Deposition
PXRD	Powder X-ray Diffractometer
TEM	Transmission Electron Microscopy
HRTEM	High Resulotion Transmission Electron Microscopy
FWHM	Full Width at Half Maximum
nm	nanometer
eV	electron volt

LIST OF SYMBOLS

d	Inter layer spacing of the crystal
λ	Wavelength
n	Layer of plane
θ	Angle
D	Crystallite size
K	Constant
β	Line broadening at half the maximum height
E_g	Band gap energy
h	Planks constant

CHAPTER 1

INTRODUCTION

This Chapter presents a brief introduction of the nanomaterial that is, TiO_2, Mn doping in TiO_2 and also photoluminescence and hydrothermal method. This follows by the statement of problems, objectives and scope of the research.

1.1 Nanomaterial

Nanomaterials research is an area that has a material science approach in nanotechnology. The size of nanomaterials is less than 100 nanometers. The important reasons that nanomaterials are interesting to be studied are optical, magnetic, electrical and other properties of these materials which are different or even improved in comparison with their bulk. These properties are being used to great impacts in electronics, medicine and other applications. These interesting properties resulted from their nanometer size that made them to have: (i) larger part of surface atoms; (ii) higher surface energy; (iii) space containment (spatial confinement); (iv) lower defect (reduced imperfections) (Alagarasi, 2011).

1.2 TiO_2 nanomaterials

Titanium dioxide (TiO_2) is being extensively used due to its good photocatalytic properties, nontoxicity and, wide applications to solve environmental problems such as photocatalyst, cancer treatment, photonic crystals, UV blockers and, self-cleaning materials (Peining et al., 2011). TiO_2 is also one of the potential candidate for solar energy application because of the special optoelectronic and photochemical properties of TiO_2 (Lucky, 2008).These applications originated from the specific electronic and ionic properties of TiO_2 which strongly depend on the specific crystal structure (anatase, rutile, or brookite) and its morphology, i.e. titanium dioxide is a photocatalytic material that has different nature of the valence and conduction bands compared of the semiconductor metal oxides. The band gap energy of TiO_2 nanostructure is much higher than that of bulk TiO_2 (Bauer et al., 2011).

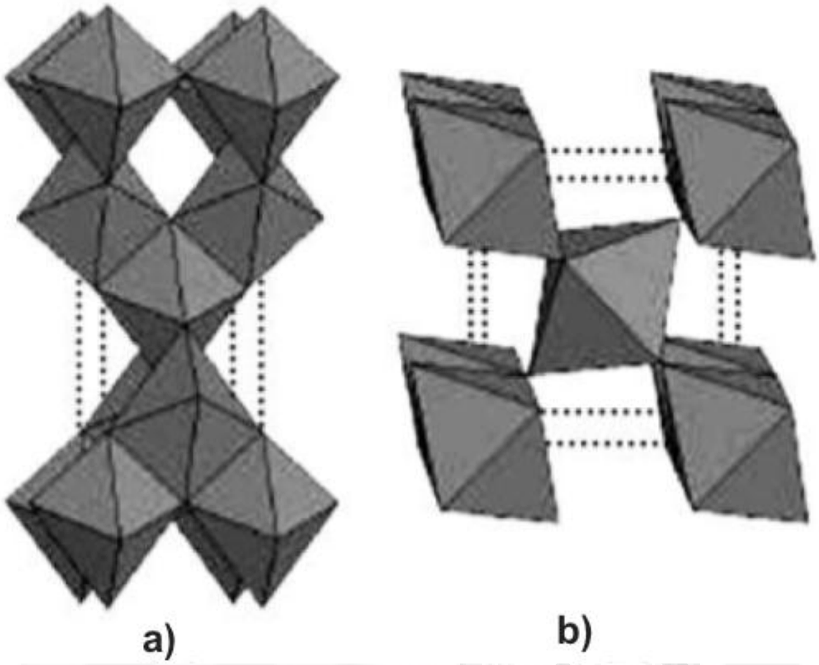

Figure 1.1. Crystalline structure of a) anatase and b) rutile phases of TiO_2

Both the anatase and rutile have same tetragonal crystalline structure with different volume which the anatase unit cell has higher volume than the rutile. Figure 1.1 presents crystal arrangements of two phases of TiO_2 (Kiatkittipong, 2012). The band gap of the rutile form is 3.02 eV with the absorption edge at 416 nm that is in the visible area. The band gap of the anatase form is 3.20 eV with the absorption edge in the near UV area at 386 nm (Bannerji et al., 2006).

1.3 Mn Doping with TiO_2

The electron is excited from the valence band to the conduction band and leaves a hole in the valence band when a semiconductor is illuminated by light of energy higher than its band gap. TiO_2 can be excited by UV light due to its wide band gap (3.2 eV for anatase phase). The practical applications of TiO_2 are limited in most conditions because of its wide band gap. The band gaps of TiO_2 were narrowed by doping the compounds with metal (such as Fe, Cr, Co, Mn, V, and Ni) or nonmetal atoms (Figure 1.1). Manganese (Mn) is the most potential material to permit the important optical absorption in the visible or even the infrared solar light between the 3d metals. The optical absorption energy of TiO_2 is increased from the limited ultraviolet spectral range well into the major visible and even infrared range by doping Mn with TiO_2 (Deng et al., 2011; Yahya, 2010).

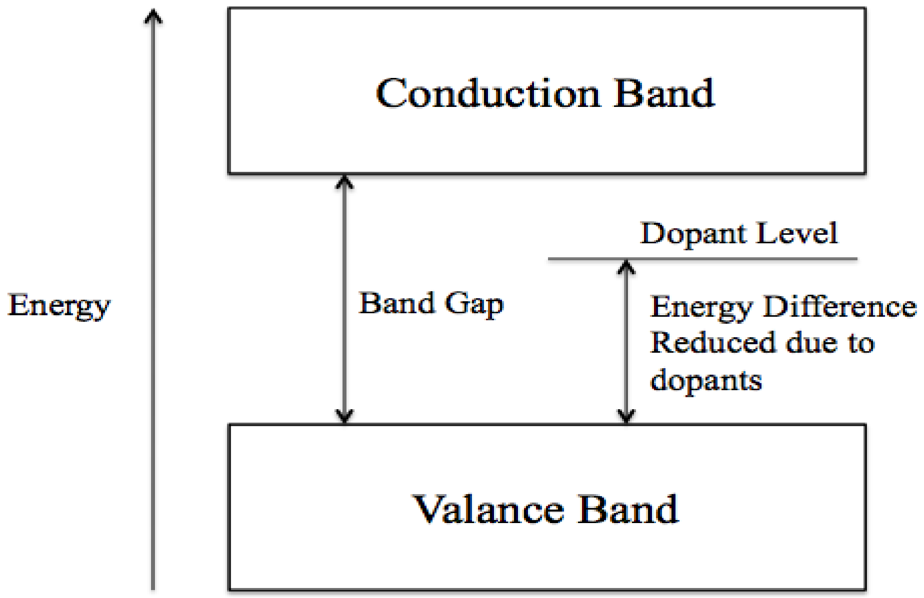

Figure 1.2. Schematic diagram of TiO_2 doped with transition metal

1.4 Hydrothermal synthesis of nanomaterials

Nowadays considerable studies have denoted hydrothermal route as a powerful and encouraging method for preparing 1-D nanomaterials, such as nanowires and nanotubes. Since it is a simple procedure and low cost, it can be beneficial and would be worthwhile to use hydrothermal reactions for the synthesis of nanostructures (Zhao et al., 2007). Apparently, the morphologies of the obtained TiO_2 nanostructure, synthesized by hydrothermal treatment, can be controlled by changing the structure (or size) of raw material, the species and concentration of alkaline solution, reaction temperature and time (Jitputti et al., 2008). Hydrothermal process occurs in the aqueous solutions at temperatures higher than 100 ºC and high pressures to produce various chemical compounds and materials.

The pH of the medium, the duration and temperature of synthesis, and the pressure in the system are the main parameters of hydrothermal synthesis to explain the properties of resulting products and the processes kinetics. The autoclaves which sealed in steel cylinders that can bear high pressure and temperature for a long time is used to carry out the synthesis.

Hydrothermal synthesis provides effective control of the size and shape of nanostructures at relatively low response temperatures and short response times, providing for well crystallized response products with a high uniformity and definite composition. Hydrothermal synthesis is a profitable method for the commercial synthesis of nanostructures (Almeida, 2010).

1.5 Photoluminescence

Photoluminescence (PL) is the phenomenon of certain types of materials on exposure to UV or visible light, without the involvement of the heat generation. The principles of PL is schematically shown in Figure 1.2 When the kinetic energy of the electrons in the molecule are increased by lighting, electrons move from the base state (valance band) S0 to the excited states (conduction band) S1. Electrons release the absorbed energy in the form of heat or light, when they will return to the valance band. The light that electrons give off when they return to valance band is known as PL (Chuanwang, 2004).

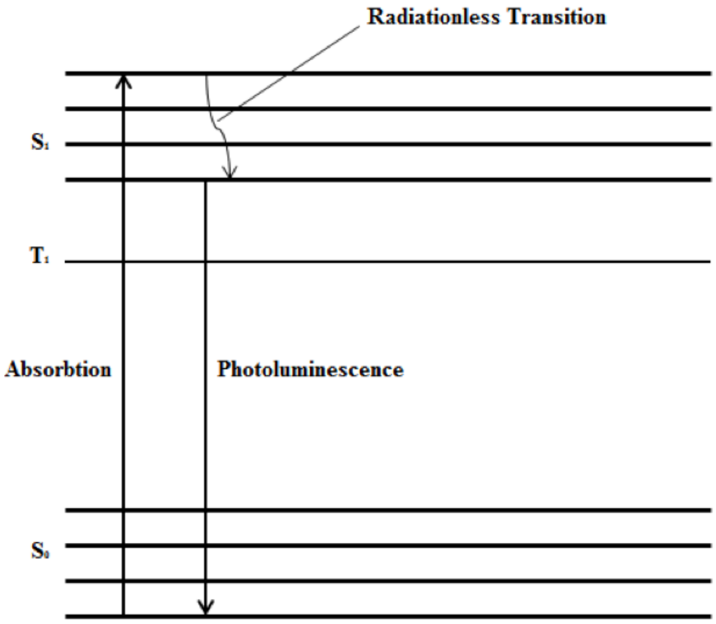

Figure 1.3. Schematic diagram of absorption and emission of photon by electron in atom

1.6 Photoluminescence properties of TiO_2 nanomaterials

The optical properties of a material are associated with the band gap energy and band structure, which in turn depend on the crystal structure of material (Leweyehu, 2009). The PL signals which can display behavior of photo-induced electrons and holes are useful since the signals can explain the recombination of photo-induced electrons and holes in TiO_2. The nanostructured TiO_2 powder shows obvious PL bands in visible light (Liu et al., 2007).

1.7 Magnetic properties of Mn

Ferromagnetic materials are divided to two groups such as soft magnetic materials and hard magnetic materials. Soft magnetic materials can be demagnetized at low magnetic field it means coercivity H_c of soft magnetic materials is low. The permeability of soft magnetic materials is high because they can be easy magnetized. Soft magnetic materials can be suitable for applications of recording heads and magnetic cores. The coercivity H_c of hard magnetic materials is high because high magnetic field is required to demagnetize. The soft magnetic materials are useful for applications of permanent magnets and magnetic recording media.

Mn is a magnetic material that can be classified as soft ferromagnetic material. Mn has important magnetic properties such as high permeability, high saturation induction and low coercive force. Technical applications of newly were developed soft ferromagnetic involve the changes in magnetization that occur easily in weak magnetic fields (Magnetic Materials Unit, 2014).

1.8 Problem statement

TiO_2 is an important material for application in photocatalysis, solar-photovoltaic, ceramic material, filler, coating, pigment and cosmetics. There are many different shapes of TiO_2 such as nanoparticles, nanotubes, nanorods and nanowires, have been reported. Nanomaterials with various shape and structure usually have different optical and electrical properties (Kavitha et al., 2013).

The major problem facing in the fabrication of TiO_2 nanostructure is about the control of the size and shape of the material which have directly effect on it's physical properties. The nanostructures prepared by hydrothermal method shows better structural, morphological and photocatalytic property (Kavitha et al., 2013).

Hydrothermal technique is a powerful method to prepare 1-D nanomaterials, such as nanowires and nanotubes. Therefore hydrothermal reaction is very beneficial for the synthesis of TiO_2 nanostructures.

1.9 Objectives of research

The present study aims to investigate the fabrication of TiO_2 nanostructure by using hydrothermal method. The main objective of the work is to present a systematic study on the growth, physical and optical characterization of TiO_2 nanostructures prepared by hydrothermal method. Moreover, the study also aims to experimentally study about the effect of Mn doping on structural and photoluminescence properties of TiO_2 nanostructures. More specifically the study pursues the following objectives;

(1) To investigate of morphology and photoluminescence properties of TiO_2 nanostructure fabricated by hydrothermal technique.

(2) To investigate of the effect of Mn doping on morphology, structure and photoluminescence properties of TiO_2 nanostructure prepared by hydrothermal technique.

1.10 Scope of research

The fabrication and photoluminescence properties of TiO_2 nanostructures by hydrothermal method using EN and TH were investigated in this study. This dissertation also studied about the effect of Mn doping in TiO_2 and the photoluminescence properties of it. The magnetic behavior of Mn doped in TiO_2 was investigated from VSM result.

1.11 Outline of dissertation

The dissertation is structured in five chapters. The current Chapter (Introduction) presents the background of the study, research questions, statement of the problem, theoretical framework, objectives and scope of the study and outline dissertation. Chapter 2 reviews the previous work on hydrothermal fabrication technique and photoluminescence study of TiO_2 nanostructures. Chapter 3 is devoted to description of experimental methods that have been used for preparation of nanomaterials. Chapter 4 presents our obtained results from fabrication and characterization of TiO_2 nanostructures. Finally, chapter 5 concludes the research.

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