UNIVERSITI PUTRA MALAYSIA

SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYSTIC ACTIVITY OF MULTIWALLED CARBON NANOTUBES/ TITANIUM DIOXIDE NANOCOMPOSITE

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By

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

June 2015

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

SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYSTIC ACTIVITY OF MULTIWALLED CARBON NANOTUBES/TITANIUM DIOXIDE NANOCOMPOSITE

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June 2015

Chair: Professor Elias Saion, PhD
Faculty: Faculty of Science

As a result of large band gap and high recombination of photo-generated electrons-holes within nanoseconds, which limit the effectiveness of anatase-phase titanium dioxide (TiO_2) semiconductor nanoparticle. Active MWCNTs/TiO_2 nanocomposites were fabricated by dispersing TiO_2 onto the surface of functionalized multiwalled carbon nanotubes (fMWCNTs) and used it as a photocatalyst. The optical, structural, and morphological properties of the as-prepared MWCNTs/TiO_2 nanocomposites were studied. The typical particle sizes between 30 and 36 nm were achieved by TEM. This was supported by the crystal sizes of 16, 14 and 13 nm for MWCNTs/TiO_2 ratios of (1:3), (1:2), and (1:1) respectively, evaluated from Shearer equation of the XRD spectra, which show the present of anatase and rutile states. The optical properties were characterized using UV-Vis reflection spectroscopy and found the band gap of 2.93, 2.86, and 2.75eV for MWCNTs/TiO_2 ratios of (1:1), (1:2), and (1:3) respectively, calculated from Kubelka-Munk function. The PL peak intensity of TiO_2 was higher for MWCNTs/TiO_2 (1:3) as loading of TiO_2 increased. The effect of the initial concentration of the methylene blue dye and pH of the medium were investigated on photocatalytic activity of the MWCNTs/TiO_2 nanocomposites of the lowest band gap at the optimum mass ratio (1:3). It was found that the photodegradation followed the first order kinetics. The photocatalytic activity was found to increase with increase in the initial dye concentration after which it falls as the concentration of methylene blue is increased above optimum. At 30 min, 92.56 and 75.95% degradation efficiency were recorded for 10.2 and 7.0 pH solutions respectively. While in 1.9 pH solution, approximately 45.23% methylene blue degradation was recorded.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Sarjana Sains

PENYEDIAAN, PENCIRIAN, DAN APLIKASI POTOMANGKIN NANOKOMPOSIT KARBON NANOTIUB PELBAGAI DINDING/TINTINUM DIOKSIDA

Oleh

NURA ABDULLAHI

June 2015

Pengerusi: Professor Elias Saion, PhD
Fakulti: Sains

Hasil daripada jurang jalur besar dan penggabungan semula tinggi sesuatu gambar yang dihasilkan elektron-lubang dalam nanosaat, yang menghadkan keberkesanan anatase fasa titanium dioksida (TiO_2) semikonduktor nanopartikel. MWCNTs aktif / nanokomposit TiO_2 telah dipalsukan oleh menyuraikan TiO_2 ke permukaan fMWCNTs karbon multiwalled (MWCNTs) dan menggunakannya sebagai fotomangkin a. Sifat-sifat optik, struktur, dan morfologi sebagai disediakan-nanokomposit MWCNTs/TiO_2 telah dikaji. Saiz zarah yang biasa antara 30 dan 36 nm telah dicapai oleh TEM. Ini disokong oleh saiz kristal 16, 14 dan 13 nm untuk MWCNTs/TiO_2 nisbah (1:3), (1:2), dan (1:1) masing-masing, dinilai daripada persamaan Shearer spektra XRD, yang menunjukkan semasa anatase dan rutil negeri. Ciri-ciri optik telah dicirikan menggunakan UV-Vis refleksi spektroskopi dan mendapati jurang jalur daripada 2.93, 2.86, dan 2.75eV untuk MWCNTs / nisbah TiO_2 dari (1:1), (1:2), dan (1:3) orang, dikira dari fungsi Kubelka-Munk. PL keamatan puncak TiO_2 adalah lebih tinggi untuk MWCNTs/TiO_2 (1:3) sebagai pemuatan TiO_2 meningkat. Kesan kepekatan awal pewarna metilena biru dan pH medium disiasat aktiviti fotopemangkinan daripada nanokomposit MWCNTs/TiO_2 jurang band yang paling rendah pada nisbah jisim optimum (1:3). Ia telah mendapati bahawa Pemfotorosotaan diikuti kinetik peringkat pertama. Aktiviti fotopemangkinan didapati meningkat dengan peningkatan kepekatan pewarna awal selepas itu ia jatuh sebagai kepekatan metilena biru meningkat di atas optimum. Pada 30 min, 92.56 dan 75.95% degradasi dicatatkan bagi penyelesaian 10.2 dan 7.0 pH masing-masing. Ketika di 1.9 pH penyelesaian, kira-kira 45.23% metilena biru degradasi dicatatkan.

ACKNOWLEDGEMENTS

Praise be to Allah the beneficent and merciful for his infinite mercy upon successful accomplishment of this research work. I would like to extend my sincere appreciation to my supervisor, Prof. Dr. Elias Bin Saion, for his tolerance, tireless supervision and encouragement throughout the research period. I am highly indebted to his monumental effort in introducing me to nanoscience and nanotechnology. His expertise in this discipline has really inspired me to pursue my future academic carrier in this unique field. This research would not have been completed impeccably without his guidance, constructive critism and amiable supervision.

I would also like to use this medium in extending my profound appreciation to the member my supervisory committee in person of Prof. Dr. Abdul Halim Shaari who was ever ready to give supports at all cost till the end of this study. I thank him immensely for his perusal and thorough reading of my thesis and valuable suggestions. Appreciation is also given to all members of staff of physics department of Faculty Science and Institute of Biological Sciences (IBS) Universiti Putra Malaysia for their assistance and help. I would also like to express my deepest gratitude to all my friends and colleagues, Naif Mohammed Al-Hada, Aysar keteib and Abdullahi Makama, amongst others for their cooperation and cordial relationship.

This acknowledgement is incomplete without the love, prayers, caring and encouragement from my parents Alh. Maikano Yahaya and Haj. Aishatu Abdullahi, my wives, brothers and sisters and all my entire family members.
Without their constant support and inspirations all my efforts might have been futile.

June 2015

I certify that a Thesis Examination Committee has met on 10 June 2015 to conduct the final examination of Nura Abdullahi on his thesis entitled "Synthesis, Characterization and Photocatalystic Activity of Multiwalled Carbon Nanotubes/Titanium Dioxide Nanocomposite" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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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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LIST OF SYMBOLS

CNT	Carbon nanotube
eV	Electron volt
f	Frequency
MWCNTs	Multi walled carbon nanotubes
R	Removal efficiency
TiO2	Titanium dioxide
OC	Degree Celsius
h	Plank Constant

LIST OF ABBREVIATIONS

FESEM	Field emission scanning electron microscope
FTIR	Fourier transforms infrared spectroscopy
PL	Photoluminescence spectroscopy
TEM	Transmission electron microscopy
UV-vis	Ultraviolet visible
XRD	X-ray diffraction
K	First order rate constant
MB	Methylene blue
KM	Kubelka–Munk
PPM	Part Per Million

CHAPTER 1

NANOMATERIAL AND NANOTECHNOLOGY

1.1 Introduction

A material is said to be "nano" if it has at least one dimension that is less than100 nanometer. Nanomaterials can have various structures including 0-D structure of quantum dots of atomic clusters, 1-D structure of nanotubes and nanorods or 2-D structure of nanofilms. The studies of nanostructures can be viewed in two fundamental ways, i.e. the nanoscience and nanotechnology (Bandaru, et al., 2005) (Bandaru et al., 2005) (Bandaru et al., 2005) (Bandaru et al., 2005) (Bandaru et al., 2005). Nanoscience enfolds the definition of fundamental aspects of nanomaterials which include the theoretical and experimental aspects, synthesis techniques and study of their properties (Krusin-Elbaum, et al., 2004) (Krusin-Elbaum et al., 2004) (Krusin-Elbaum et al., 2004) (Krusin-Elbaum et al., 2004) (Krusin-Elbaum et al., 2004). Starting from nanoscaled structures, scientists restructure them and then assemble functional systems that can be integrated in to the products with unique properties classified by the size of the nanomaterials being developed and used, not by the process being used or product being produced (Drexler, 1986) (Drexler, 1986) (Drexler, 1986) (Drexler, 1986) (Drexler, 1986). While nanotechnology is the term used collectively for the application aspect involved in the manipulation of matter which also includes the development and commercialization of nanoscale materials.

Nanomaterials became the concept of interest since the introduction of nanotechnology. The influence of this field to both science and industrial applications has been so important and is still developing. Nanotechnology is a highly interdisciplinary field of research and a cutting-edge involving numerous disciplines such as applied physics, chemistry, material science, interface and colloid science, device physics, molecular biology, chemical engineering, mechanical engineering and electrical engineering, to mention a few (Yang, 2009). Nanoscience, therefore, can possibly be regarded as an extension of the existing natural sciences into nanoscale dimension, or as a recasting of existing sciences using a newer, more modern term.

Synthesis and characterization of nanomaterials play monumental role in research and development of nanomaterials. Based on synthesis, there are two main approaches for assembling nanomaterials, namely the top-down and the bottom-up. In the top-down synthesis approach nanomaterials are produced from large size objects without moleculer level control (Yang, 2009). The bottom-up approach is the technique where materials and devices are built from a few molecule components by chemical self-assembling in solution into functional superstructures (Yang, 2009). The top-down approach is mostly used in industries due to its simplicity and fast processing time, however, in the case of producing less than 100 nm nanomaterials, costs of production and time increased greatly. Other drawbacks include limited control of morphology and huge defects on the surfaces of nanomaterials.

Consequently, the "bottom-up" approach has become the alternative approach being actively investigated.

Nanosized titanium dioxide (TiO_2) is one of the most studied photocatalyst. The enhanced photoactivity of nanosize TiO_2 is attributed to the high surface area and electronic quantization effects. The former property exposes more area of the particles to the light illumination and reacting surfaces making the photocatalystic process occur faster due to generation of more free radicals that are responsible for the efficient degradation. While the latter produces an increase in the absorption coefficient at specific wavelengths of light.

In an attempt to increase the overall photoactivity of TiO_2 various modifications were reported such as addition of sacrificial agents (oxalic acid, formic acid and formaldehyde) acting as electron donors (Li et al., 2003), addition of carbonate salt (Sayama and Arakawa, 1992, 1997), transitional metal ion doping and rare earth metal ion doping (Wang et al., 2004) noble metals loading on the semiconductor (Abrahams et al., 1985; Sadeghi et al., 1996; Sakata et al., 1982).

In the quest for more viable, benign and cost effective alternatives fabrication of CNTs/TiO_2 have considerably grown due to the unique and outstanding properties of CNTs. CNTs are endow with strong covalent bonding, unique exceptional properties such as tensile strength, high resilience, high current carrying capacity as well as high thermal conductivity.

In the fabrication of CNTs/TiO_2 photocatalyst , functionalized CNTs is used as a substrate to control the morphology of TiO_2 dispersed on its surfaces. The synergic effect driven from both materials is believed to have influence in red shifting the absorption band gap edge of TiO_2 to enhance its response in the visible portion of the spectra and increase the surface area of the prepared composites, which is one of the important parameters in photocatalysis. The CNTs also act as an electron acceptor to prevent recombination of photo generated holes and electrons, generating more radicals and oxidants.

1.2 Problem Statement

The most widely researched photocatalyst of all is TiO_2 due to its low cost, environmentally friendly, inertness, abundance and non-corrosiveness. However, its large band gap energy that prevents visible light harness capability, very fast thermal influenced electron-hole recombination taking place within nanoseconds, and generating unwanted heat or photons have limits its effectiveness (Minero and Vione, 2006). Decoration of TiO_2 on a carbonaceous substrate such as multi-wall carbon nanotubes (MWCNTs) could enhance the photoactivity in a number of ways: by (1) acting as a reservoir for electrons to enhance photo-induced charge separation and increase the lifetime of separated charges; (2) serving as a surface impurity dopant to reduce band gap energy; and (3) forming Ti−O−C or Ti−C defect sites that enable visible light absorption and photoreactivity to occur (Sun and Wang, 2013; Woan et al., 2009; Zhang et al., 2010).

Many literatures have reported different techniques for the synthesis of $MWCNTs/TiO_2$ nanocomposite and its photoactivity. However most of these techniques are difficult, costly, generate impurities, and require multiple steps and high reaction temperatures leading to the damage in the CNT structure.

In this work we have device a simple method of covalent attachment of TiO_2 onto acid treated MWCNTs under mild reaction condition (at 70 ^oC and 30 min) and obtained visible light active $MWCNTs/TiO_2$nanocomposites.

1.3 Research Objectives

The research is aimed at synthesis, characterization and photocatalystic activity of $MWCNTs/TiO_2$ nanocomposite. The activities of the catalysts will be tested using degradation of methylene blue dye within visible light spectrum. The specific objectives to be achieved are:-

1. To synthesize $MWCNTs/TiO_2$ nanocomposite of different mass ratios as visible light responsive photo-catalysts.

2. To investigate the optical, structural, and morphological properties of the as-prepared $MWCNTs/TiO_2$ nanocomposites.

3. To study the effects of mass ratios of $MWCNTs/TiO_2$, initial concentration of methylene blue dye and pH of the medium on photo-catalytic activity of the nanocomposites.

1.4 Scope of the research

The research was designed to employ simple approach in the synthesis of $MWCNTs/TiO_2$ nanocomposite. Despite numerous applications of these composite, the work is restricted to their photocatalystic application in the degradation of organic pollutant precisely methylene blue via visible light irradiation. The research was also confined to the effect of initial dye concentration, the effect of pH of MB aqueous solution and the effect of $MWCNTs/TiO_2$ mass ratios on the photocatalystic activities of the nanocomposites.

1.5 Significance of the research

Much interest is driven towards nanostructured materials by the virtue of their unique optical and electrical properties. Currently synthesis, characterization and application of $MWCNTs/TiO_2$ photocatalysts have grown significantly. $MWCNT/TiO_2$ composites photo-catalysts have peacefully demonstrate efficiency in the degradation of organic dyes using solar spectrum into harmless and biodegradable compounds. A number of essential features have extended the viability of $MWCNTs/TiO_2$ photocatalyst in the degradation of contaminated water, such as; (i) ambient operating temperature (normally operated at room temperature) and pressure, (ii) environmentally friendly i.e. mineralization of parents and their intermediate compounds completely without generation of secondary pollutants and (iii) cost effective. Other opportunities that could be potentially extracted from MWCNTs/TiO_2 photocatalysts may include hydrogen generation from water splitting reaction, photovoltaic cell, CO_2 conversion to liquid fuel and many more.

1.6 Thesis outline

Synthesis, characterization and photocatalystic activity of MWCNTs/TiO_2 nanocomposites are the main features of evaluation in this thesis. In chapter one summary on TiO_2 nanoparticles as photocatalyst, in addition to the statement problem, significance of the study, scope and objectives of the research were stated. A brief discussion on the synthesis method, characterization and photodegradation efficiency of MWCNTs/TiO_2 photocatalyst was presented in Chapter 2. In chapter 3, the optical absorption, band gap energy of TiO_2, quantum confinement of nanomaterials and density of states were discussed. The comprehensive and detailed preparation technique and photodegradation experiments were explained in chapter 4. The results and discussion for every characterization technique used was provided in chapter 5 which include Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy, X-ray powder diffraction (XRD), transmission electron microscopy (TEM), ultra violet visible spectroscopy (UV-vis.) and photoluminescence spectroscopy (PL). Chapter 6 gives the summary and conclusions of the research work as well as suggestions for future work. The final section of the thesis, itemize references, publications and conferences attended by the author.

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LIST OF PUBLICATIONS

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