UNIVERSITI PUTRA MALAYSIA

STRUCTURAL AND OPTICAL PROPERTIES OF TiO_2 AND ZrO_2 NANOPARTICLES AND $Ti_XZr_{1-X}O_2$ NANOCOMPOSITES IN RELATION TO THERMAL-TREATMENT METHOD

AYSAR SABAH KEITEB

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By

AYSAR SABAH KEITEB

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

November 2016

DEDICATION

"and of knowledge ye have been vouchsafed but little"
Holy Qur'an

"The significant problems we face can't be solved by the same level of thinking that created them"
Albert Einstein

To my beloved parents and wife for their endless help, encourage & support

Thank you for everything

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

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November 2016

Chairman : Professor Elias Saion,PhD
Faculty : Science

Metal oxide nanoparticles hold a great scientific and technological interest due to their unique physical and chemical properties arise from their nanoscale dimension and large number of surface atoms. As their properties are dependent on large surface area to volume ratio and quantum confinement effect, they have potential applications in almost every field of technology. Several methods have been employed previously to synthesize metal oxide nanoparticles with enhanced chemical and physical properties. However, most of these methods have used a complicated procedure, longer reaction times, employed toxic reagents and produced by-products which are not environmentally friendly. Current study employed thermal treatment method to prepare TiO_2 and ZrO_2 nanoparticles and $Ti_x Zr_{1-x}O_2$ nanocomposites (x= 0.9, 0.7, 0.5 0.3 and 0.1) directly from surfactant solution without any drying prior to calcination process. An aqueous solution contains of metal precursors, poly(vinyl) pyrrolidone as a capping agent and deionized water as a solvent. The precursors solution underwent calcination at temperatures ranging from 500 to 800 ^oC. The physical structural, elemental composition, phase composition, morphological and optical properties of the synthesized nanoparticles/nanocomposites were investigated using energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), and UV-Vis spectrometer. A thermogravimetric analyzer (TGA) was used to study thermal stability and the removal of polymer from the samples while being calcined. Full decomposition of the polymer was found at 488 ^oC. The FTIR results confirmed the removal of the polymer along with organic matter and the existence of metal oxide nanoparticles at 500-800 ^oC. The elemental composition of the sample obtained by EDX spectroscopy has confirmed the formation of $Ti_x Zr_{1-x}O_2$ nanoparticles. The XRD diffraction patterns at calcination temperatures 500-800 ^oC showed that the crystallite sizes for TiO_2 nanoparticles were in the range of ~5–27 nm with tetragonal structure, ~4-16 nm with a face-centered cubic structure for ZrO_2 nanoparticles and in the range of 5-23 nm for tetragonal mixed cubic structure of $Ti_x Zr_{1-x}O_2$ nanocomposites. These results were

further proved by TEM results which showed that the formation of metal oxide has taken place in nanoscale size. The optical band gap of the samples calculated using Kubelka-Munk equation varied from 3.55 to 3.40 eV for TiO_2 nanoparticles, 4.88 to 4.71 eV for ZrO_2 nanoparticles, and 5.21-3.50 eV for $Ti_x Zr_{1x}O_2$ nanocomposites and calcination temperatures 500-800 ^oC. This is the results of the average particle sizes determined by TEM images, which were found to be increasing with increased calcination temperatures from 6 to 30 nm for TiO_2 nanoparticles, 5 to 18 for ZrO_2 nanoparticles and 4-25 nm for $Ti_x Zr_{1-x}O_2$ nanocomposites. The reason for this is that the quantum confinement effect takes place whereby for the smaller particle size, the interaction between outer electrons and ions (protons) is weaker that leads to larger band gap energy and for the larger particle size the interaction between outer electrons and ions (protons) is stronger that leads to smaller band gap energy.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

CIRI STRUKTUR DAN OPTIK NANOPARTIKEL TiO_2 DAN ZrO_2 DAN NANOKOMPISIT $Ti_XZr_{1-X}O_2$ DISINTISIS DENGAN KAEDAH RAWATAN TERMA

Oleh

AYSAR SABAH KEITEB

November 2016

Pengerusi : Profesor Elias Saion,PhD
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Partikel nano logam oksida mempunyai kepentingan sains dan teknologi yang besar kerana sifat-sifat fizikal dan kimia yang unik timbul dari dimensi nano dan bilangan atom permukaan yang banyak. Sebagai sifat-sifat yang bergantung kepada nisbah luas kawasan permukaan kepada jumlah isipadu yang besar dan kesan ruang terkuantum, mereka mempunyai potensi aplikasi dalam hampir setiap bidang teknologi. Beberapa kaedah telah digunakan sebelum ini untuk mensintesis nanopartikel logam oksida dengan dipertingkatkan ciri-ciri kimia dan fizikal. Walau bagaimanapun, kebanyakan kaedah-kaedah ini telah menggunakan prosedur yang rumit, masa tindak balas lebih lama, menggunakan reagen toksik dan menghasilkan produk sampingan yang tidak mesra alam. Kajian semasa adalah menggunakan kaedah rawatan terma untuk menyediakan nanopartikel TiO_2 dan ZrO_2 dan nanokomposit TiO_x $Zr_{1-x}O_2$ (x = 0.9, 0.7, 0.5 0.3 dan 0.1) terus dari larutan sufkaten tanpa pengeringan terlebih dahulu sebelum proses pengkalsinan. Larutan akueus mengandungi prekursor logam, poli (vinil) pyrrolidone sebagai ejen penyalut bahan dan air ternyahion sebagai pelarut. Larutan prekursor menjalani pengkalsinan pada suhu antara 500-800 ^{o}C. Struktur fizikal, komposisi unsur, komposisi fasa, sifat morfologi dan optik nanopartikel / nanocomposites yang disintesis telah diselidik menggunakan spektroskopi serakan tenaga X-ray (EDX), spektroskopi inframerah jelmaan Fourier (FT-IR), mikroskop electron imbasan ruang emisi (FESEM), mikroskop elektron penghantaran (TEM), serbuk pembelauan sinar-X (XRD), dan spektrometer UV-Vis. Penganalisis termogravimetri (TGA) telah digunakan untuk mengkaji kestabilan haba dan penyingkiran polimer dari sampel ketika proses pengkalsinan sedang dijalankan. Penguraian penuh polimer ditemui pada 488 ^{o}C. Keputusan FTIR mengesahkan penyingkiran polimer bersama-sama dengan bahan organik dan kewujudan nanopartikel logam oksida pada suhu pengkalsinan 500-800 ^{o}C. Komposisi unsur sampel yang diperolehi oleh spektroskopi EDX telah mengesahkan pembentukan nanopartikel Ti_x $Zr_{1-x}O_2$. Corak pembelauan XRD pada suhu pengkalsinan 500-800 ^{o}C menunjukkan bahawa saiz kristal untuk nanopartikel TiO_2 adalah dalam lingkungan ~ 5-27 nm dengan struktur tetragonal, untuk nanopartikel ZrO_2 ialah ~ 4-

16 nm dengan struktur pepejal berpusat muka dan untuk nanokomposit $Ti_x Zr_{1-x}O_2$ ialah dalam lingkungan 5-23 nm dengan struktur tetragonal. Keputusan ini telah dibuktikan dengan keputusan TEM yang menunjukkan pembentukan logam oksida telah berlaku dalam saiz nano. Jurang tenaga optik sampel dikira dengan menggunakan persamaan Kubelka-Munk iaitu untuk nanopartikel TiO_2 berubah 3.55-3.40 eV, untuk nanopartikel ZrO_2 berubah 4.88-4.71 eV dan 5.21-3.50 eV untuk nanokomposit $Ti_x Zr_{1-x}O_2$ pada suhu pengkalsinan 500-800 ^oC. Ini adalah hasil daripada purata saiz zarah, yang dari imej TEM didapati semakin meningkat dengan peningkatan suhu pengkalsinan, iaitu 6-30 nm untuk nanopartikel TiO_2, 5-18 untuk nanopartikel ZrO_2 dan 4-25 nm untuk nanokomposit $Ti_x Zr_{1-x}O_2$. Ini berlaku kerana kesan ruang terkuantum di mana untuk saiz zarah yang lebih kecil, interaksi antara elektron luar dan ion (proton) adalah lebih lemah yang membawa kepada lebih besar jurang tenaga dan untuk saiz zarah yang lebih besar interaksi antara elektron luar dan ion (proton) adalah lebih kuat yang membawa kepada lebih kecil jurang tenaga.

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"In the name of Allah, the most beneficent and the most merciful"

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I certify that a Thesis Examination Committee has met on 30 November 2016 to conduct the final examination of Aysar Sabah Keiteb on his thesis entitled "Structural and Optical Properties of TiO_2 And ZrO_2 Nanoparticles and $Ti_XZr_{1-X}O_2$ Nanocomposites in Relation to Thermal-Treatment Method" 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 Doctor of Philosophy.

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

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I hereby confirm that:

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Name of Member of Supervisory Committee: Dr. Mazliana Ahmad Kamurudin

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LIST OF ABBREVIATIONS

K.M	Kubelka-Munk
DI	Deionized water
NPs	Nanoparticles
NCs	Nanocomposites
FESEM	Field Emission Scanning electron microscopy
nm	Nanometre
eV	Electron volt
θ	Bragg angle
h	Hour
min	Minutes
E_g	Optical band gap
^oC	Degree Celsius
λ	Wavelength
D	Diameter
T	Transmittance
E	Energy
B	FWHM
TiO_2	Titanium Dioxide
ZrO_2	Zirconium Dioxide
PL	Photoluminescence
A	Lattice parameter
EDX	Energy dispersive X-Ray
TEM	Transmission electron microscopy

FTIR	Fourier transforms infrared spectroscopy
XRD	X-ray diffraction
TGA	Thermo gravimetric analysis

CHAPTER 1

INTRODUCTION

1.1 Background of study

The idea of "Nano" was first introduced by Richard P. Feynman on December 1959 during an annual meeting of the American Physical Society which took place at the California Institute of Technology. In the annual meeting he introduced the idea in a speech titled "There is plenty of room at the bottom...". He stated that "I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle." Emphasis was made on the different areas where this new idea could be technically applied by Professor Feynman in the speech.

Since the 1980's, Nano-science as a field of physics has experienced significant growth (Nalwa 2004). Nano-science researches have been conducted across different disciplines like environmental science, biomedicine, engineering, agriculture, physics and medicine amongst many others. There are a number of issues related to Nano-science because of its use in hi-tech applications. Thus, the application of the basic science into applications is referred to as Nanotechnology.

The science which with matter at the scale of 1 billionth of a meter (i.e., 10^{-9} m = 1 nm) is known as Nanotechnology. Nanotechnology is also the science that manipulates matter at the atomic and molecular scale. The most important element of fabricating a nanostructure is a nanoparticle which according to Newton's law of motion is much smaller than the everyday known objects, yet larger than a simple molecule which is controlled by the mechanics of quantum (Horikoshi and Satoshi, 2013).

Nanoparticle is defined as a wide range of submicron size materials. Even though there is definition of Nanoparticles that is globally accepted, there are still different definitions of the term based on the perspective of the described material. According to the British Standards Institution, "Nanoparticles are the particles with one or more dimensions at the nano-scale". The institution further described it as dimensions of ranging from 100 nm to less than 100 nm. Specific related properties which are of novel size develop as well as materials begin the acquisition of varying elements in comparison to its molecules; this is an important length scale. Novel properties which include optical and structural properties that appear in materials that are less than 100 nm size are referred to as morphology. However, apart from "strictly Nano" (1-100 nm), particles that possess at least one dimension within scale of 1-1000 nm are referred to as nanoparticles, are widely used in the area of drug delivery (Azarmi *et al.,* 2006; Kreuter, 2007; Uchegbu *et al.,* 2013).

Some unique structural, morphological and optical properties at a nanoscale critically dependent on the size of particle, elemental features and shape might be contained in the metal oxide nanoparticle materials which are contained in semiconductors. A reduction in the size of particles makes a high surface area to the ratio of volume inevitable thereby causing an equal distribution of the particles as well as increasing the surface specific active sites for chemical reactions to improve the efficiency of absorption and reaction. The state of the surface is also increased by the surface which is enhanced- the activity of charge is changed by the surface state while conveying and influencing the dynamics of chemical reaction. Also, a reduction in the sizes of particles results into an effect of quantum size due to the limitation of charge carriers particularly the electrons. Both valence and conduction bands is being divided by the quantum size effect into different electronic states thereby making the size dependent on the band gap, the electronic and optical elements of the nanoparticles.

In this perspective, great effort has been directed towards semiconductor NPs and titanium dioxide (TiO_2) (Xiaobo and Mao, 2007). A provisional metal semiconductor which is widely used as an advanced and functional material is referred to as TiO_2 (Oana *et al.,* 2004). TiO_2 takes full advantage of its numerous elements for different applications in photovoltaics, antifogging, photocatalysis, decomposition of pollutants that are organic, sensor technology and self-cleaning agents for living environment (Pallotti *et al.,* 2015). On the other hand, another material, which has gained the interest of technologists, scientists and researchers, is Zirconia (ZrO_2). This material needs high surface area, crystalline tetragonal phase as well as an appropriate pore structure in order to be scientifically and industrially applied (Gaydhankar *et al.,* 2014).

Basically, the surface contains the large percentage of atoms that are present in nanocrystals, thus the adjustment of surface is considered one of the most accepted techniques of building nanomaterials. Apart from changing the charge, the stability of nanomaterials is enhanced is by the reactivity and functionality of nanomaterial surface. New improvement of properties can be achieved through the absorption and dispersion of inorganic and organic materials on the surface of metal oxide semiconductor nanoparticles by means of transferring charge and electronic interaction between the host semiconductor and surface attachment. This work attempts to integrate metal oxide semiconductor while investigating the structure, optical and morphological properties as-well as the use of thermal treatment for the formation of nanoparticles contained in metal oxide semiconductor.

In the present day, metal oxides nanostructures especially TiO_2 and ZrO_2 are considered as two of the most significant nanomaterials of semiconducting due to the electrical, catalytic and electronic properties they possess. An n-type semiconductor TiO_2, has a band gap of ~3.4 eV that can serve as a photocatalytic agent (Shi *et al.,* 2013). While ZrO_2 is ~ 4.7 eV band gap and is good for catalysis, oxygen sensors applications (Răileanu 2015). Also orthorhombic and cubic (fcc) structures have been displayed by $Ti_x Zr_{1-x} O_2$ nanocomposites respectively (Pfleiderer *et al.,* 2012). The binary oxides Tix Zr1-x O2 nanocomposites, are being extensively studied because of their high mechanical hardness and the fact that their properties are easy to change to suit a need; this makes them better contenders for the application.

1.2 History of Nanoscience and Nanomaterials

The history of Nano-science dates back as far as the 1920s at the time that the concept of macromolecules was developed by Herman Staudinger who later in 1953 received a Noble price. For a long time now, the use of nanoparticles has been applied in medicine and pottery. Evidence also shows that in 2500 BC. the Chinese used Gold nanoparticles as drug while India still uses Red colloidal gold in traditional medicine as Swarna Bhasma and Makaradhwaja". The use of this red colloidal gold dates back as far as 1st millennium BC (Bhattacharya and Mukherjee, 2008). Historical evidence has shown that nanoparticles of Gold-silver alloy was used for the purpose of decoration of a vessel during the Roman period (4th century AD); the vessel is called "Lycurgus Cup," and has been under the custody of the British Museum London (Freestone *et al.,* 2007). Likewise, gold trapped in the matrix of glass in its colloidal state was used in the middle ages by churches to design beautiful ruby-coloured glasses which possess various colours and hues as a result of the formation of different sizes of nanoparticle.

In the 16th Century in Europe, "Aurum Potabile" which means drinkable gold; an aqueous form of colloidal gold knowns as was believed to have healing properties for numerous diseases (Caseri, 2000). A description of techniques of synthesizing unchanging aqueous dispersions and optical elements of gold nanoparticles was given by Michael Faraday in 1857 (Faraday, 1857). In 1915 in his well-known book titled "The World of Neglected Dimensions", colloidal particles were categorized as unique matter state whose particles are too small to be detected using a microscope and at the same time not big enough to be considered as molecules, was identified by Wolfgang Ostwald.

1.3 Methods of Synthesis

Figure 1.1 is a summary of different methods of metal oxide nanoparticles preparation. The preparation of ultrafine particles involves two main approaches that have been widely accepted from time past till date. The first which is known as breakdown technique or physical approach, involves a process whereby an external force is put on a solid thereby resulting in breaking-up into smaller particles; this approach is also considered as the top-down approach. The second which is known as build-up and also referred to as bottom-up, involves the generation of liquids based on condensations of molecules or nanoparticles based on gas atoms (Horikoshi, and Satoshi 2013).

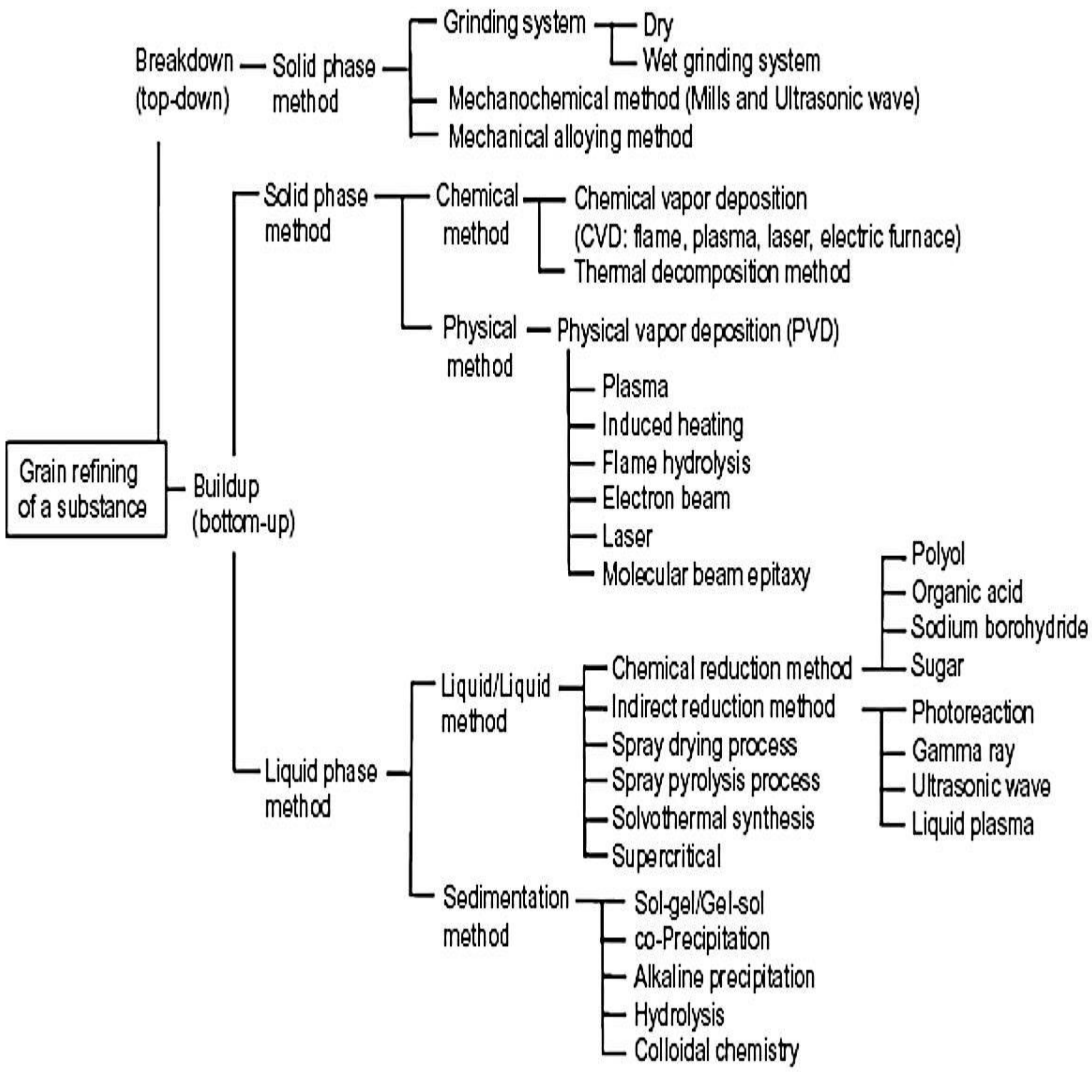

Figure 1.1 : Typical synthetic methods for nanoparticles for the top-down and bottom-up approaches (Harikoshi and Serpone, 2013).

The preparation techniques as well as other associated factors determine the use of TiO_2 and ZrO_2 and their optical properties. For the synthesis of nanomaterials which possess the needed chemical and physical properties to be possible, it is essential to prepare nanocrystals using different methods like Chemical co-precipitation method (Wei *et al.,* 2004; Fengqiu *et al.,* 2000), Hydrothermal method (Liu *et al.,* 2007; Kanade *et al.,* 2008), Precipitation method (Kim *et al.,* 1999; Wang *et al.,* 2001), Thermal decomposition (Dambournet *et al.,* 2009; Stoia *et al.,* 2013), Sol-gel method (Wei *et al.,* 2013; Gossard *et al.,* 2016), microemulsion method (Andersson *et al.,* 2002; Martínez-Arias *et al.,* 1999), Thermal evaporation (Wu et *al.,* 2005), amongst many other approaches. A substantial number of these techniques have been used in obtaining particles of desired shapes and sizes; the use of these methods could be challenging in preparingpowder form especially TiO_2 nanoparticles due to high temperatures of reaction, complex procedures, prolonged reaction time and its potential environmental harm.

1.4 Problem Statement

In recent times, the syntheses of numerous nanomaterials, which includes metals ferrite nanoparticles, have been done using thermal treatment method (Gene *et al.,* 2014; Naseri *et al.,* 2013; Naseri *et al.,* 2011) as well as other nanomaterials like zinc and cadmium oxides nanoparticles (Al-Hada *et al.,* 2013; Al-Hada *et al.,* 2014). Thermoluminescence nanomaterials also established (Erfani *et al.,* 2014). One of the popular features in the thermal treatment synthesis is the process of drying which lasts for 24 hours at a temperature of 80 ^{o}C prior to calcination. Problems of eradicating the process of drying and decreasing the consumption of energy and time by direct calcination of materials from a solution containing capping mediator and metal precursor have not been tried out in the synthesis of nanomaterials by thermal treatment method. This could improve the previous thermal treatment methods for the construction of nanostructure materials particularly metal oxide nanoparticles for the benefit of large-scale industrial use.

The main focus of this research work is to prepare size-controlled, high purity nanostructures of TiO_2, ZrO_2 nanoparticles and $Ti_x Zr_{1-x} O_2$ nanocomposites by direct calcination of a solution containing metal precursors and polymer capping in the thermal treatment method. The prepared materials undergo classification of the morphological, structural, and optical properties influenced by the concentrations of metal precursor and polymer as well as the calcination temperature.

1.5 Importance of Study

Scientific interest has been on binary metal oxide semiconductor nanocomposites and metal semiconductor oxide nanoparticles with deep investigations conducted on material science due to the physical-chemicals properties which they own as well as their variety of functions like magnetic materials, super hard metals, solar cell, catalysts, sensor, high temperature ceramics and lots more. In particular, TiO_2, ZrO_2 nanoparticles and $Ti_x Zr_{1-x} O_2$ nanocomposites are commonly used as catalytic materials, sensors and solar cell.

The present study provides a description of how TiO_2, ZrO_2 nanoparticles and $Ti_x Zr_{1-x}O_2$ nanocomposites is being synthesised through the use of thermal treatment method from an aqueous solution which is made up of poly (vinyl pyrrolidone), metal nitrates and deionized water. Prior to calcination at heat temperatures which ranged from 500 to 1000 ^{o}C, a mixture of the solution was done for 3-4 hours at 70 ^{o}C. The benefits of this method include, ease of preparation, environmental friendliness and the eradication of by-products that are not needed.

1.6 Limitation of study

This work is limited to employ metal precursors and poly(vinyl pyrrolidone) (PVP) mixed solution for the fabrication of TiO_2, ZrO_2 nanoparticles and $Ti_x Zr_{1-x}O_2$ nanocomposites. In this research work, TiO_2, ZrO_2 nanoparticles and metal oxide Ti_x

$Zr_{1-x}O_2$ nanocomposites are formulated, synthesized using thermal treatment, studied the morphological, structural, and optical properties.

1.7 Study Objectives

The main aim of this study is to generate nanoparticles which could enhance the chemical and physical properties of the bulk material by means of initiating a thermal treatment synthesis of Ti, Zr metal oxide nanoparticles and $Ti_x Zr_{1-x}O_2$ semiconductor nanocomposites in PVP modulator. The specific objectives of this study include:

I. To employ the use of thermal treatment method in the fabrication of pure TiO_2, ZrO_2 nanoparticles and $Ti_x Zr_{1-x}O_2$ semiconductor nanocomposites.
II. To investigate the influence of PVP weight concentration on the morphological, structural and optical properties of TiO_2 and ZrO_2 nanoparticles.
III. To determine the effect of various calcination temperature on the structural, morphological and optical properties of TiO_2 and ZrO_2 nanoparticles.
IV. To ascertain the impact of both calcination temperature and mixing ratios of the two metals precursors on the structural, morphological and optical properties of $Ti_x Zr_{1-x}O_2$ semiconductor nanocomposites.

1.8 Thesis Outlines

The first chapter of this thesis which is chapter one, contains the introduction which is interwoven with the background of the study, scope of the study, problem statement and objectives of the study. Chapter two consists of a review of previous studies as well as current literature in relation to the methods and background materials. Chapter three contains the theoretical background of which guides the study; this theoretical background contains various approaches and different properties which the synthesized nanomaterials possess. Chapter four which contains the methodology of the study also contains the materials, sample preparation as well as the set-up for the apparatus used in the experiments; such apparatus include FTIR, TEM, TGA, EDX, SEM, XRD, UV-Visible spectroscopy and PL. Chapter five presents the findings and discussion about the classification of metal oxide nanoparticles through the use of FESEM, XRD, TEM, EDX, FESTGA, FTIR and UV-Visible spectroscopy. The conclusions and suggestion for further research is contained in Chapter-6.

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