

**SYNTHESIS OF NANOCRYSTALLINE BISMUTH TITANATE
PHOTOCATALYSTS VIA MODIFIED HOT INJECTION METHOD**

YONG SHIH WEEN

UNIVERSITI TEKNOLOGI MALAYSIA

SYNTHESIS OF NANOCRYSTALLINE BISMUTH TITANATE
PHOTOCATALYSTS VIA MODIFIED HOT INJECTION METHOD

YONG SHIH WEEN

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For Mom, Dad, Sis, and/f/
Thank you for your everlasting love and support

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ABSTRACT

Nanocrystalline bismuth titanate materials were successfully synthesized via modified hot injection method. The modified method used aqueous solution of nitric acid instead of non coordinating solvent as the reaction solvent which allowed a lower reaction temperature at 130°C. XRD and FESEM analyses showed that the synthesized material crystallized in a cubic structure with *Fm3m* space group with average particle size of 7.9 nm. The effect of heating temperature showed that bismuth titanate with two space groups of *Fm3m* and *I23* were obtained after heating at 400°C for 3 hours. Interestingly, the mixed phase bismuth titanate materials have the lowest band gap energy of 2.57 eV and they showed the highest photocatalytic activity in phenol degradation UV light for 12 hours. The effect of ageing time on physico-chemical properties showed particle size of the materials increased with increasing of ageing time. As a result, bismuth titanate with 2 hours of ageing time was the best photocatalyst due to its small particle size of 6.4 nm. Similarly, surfactant content used did not affect phase formation of the materials but affected the particle size. The highest surface area of 20.2 m²/g was observed in the bismuth titanate material synthesized using oleic acid to bismuth mole ratio of 1.46:1 and it had contributed to its high photocatalytic activity of 87% phenol degradation. In order to further examine the photocatalytic activity of the nanocrystalline bismuth titanate, bismuth titanate of different bismuth to titanium mole ratios (10:1 to 18:1) were synthesized. XRD results strongly suggested the formation of solid solution as all the materials crystallized in cubic structure with *Fm3m* space group. Bismuth titanate with bismuth to titanium mole ratio of 10:1 has achieved the highest phenol degradation percentage of 88% due to smaller particle size as well as higher mole ratio of titanium content in the material.

ABSTRAK

Bismut titanat berhablur nano telah berjaya disintesis melalui kaedah sintesis suntikan panas yang diubahsuai. Kaedah terubah suai menggunakan larutan akueus asid nitrik untuk menggantikan pelarut bukan koordinasi sebagai pelarut tindak balas bagi mengurangkan suhu tindak balas kepada 130°C. Analisis XRD dan FESEM menunjukkan bahan yang disintesis berhablur dalam sistem kiub dengan kumpulan ruangan $Fm3m$ dengan purata saiz zarah sebanyak 7.9 nm. Kesan pemanasan menunjukkan bismut titanat wujud dalam dua fasa kumpulan ruangan iaitu $Fm3m$ dan $I23$ selepas dipanaskan pada 400°C selama 3 jam. Menariknya, fasa campuran bismut titanat tersebut mempunyai leluang jalur tenaga yang rendah iaitu 2.57 eV, lalu menunjukkan kadar fotodegradasi fenol yang tinggi di bawah sinaran UV selama 12 jam. Kajian kesan masa penuaan terhadap ciri-ciri fizikal-kimia menunjukkan saiz zarah bahan meningkat dengan peningkatan masa penuaan. Oleh yang demikian, bismut titanat dengan 2 jam masa penuaan sahaja adalah fotomangkin terbaik disebabkan saiz zarah yang kecil iaitu 22 nm. Seperti kesan masa penuaan, kuantiti surfaktan tidak mempengaruhi pembentukan fasa tetapi memberi kesan terhadap saiz zarah. Luas permukaan tertinggi sebanyak 20.2 m²/g yang diperolehi pada bismut titanat yang disintesis menggunakan nisbah mol asid oleik kepada bismut 1.46:1, seterusnya menyumbang kepada aktiviti fotomangkin yang tinggi iaitu 87% dalam fotodegradasi fenol. Demi meningkatkan lagi aktiviti fotomangkin, bismut titanat yang berbeza nisbah mol bismut kepada titanat (10:1 hingga 18:1) telah disintesis. Corak XRD menunjukkan pembentukan pepejal larutan dalam semua bahan yang disintesis berhablur dalam sistem kiub dengan kumpulan ruangan $Fm3m$. Bismut titanat dengan nisbah mol bismut kepada titanat 10:1 mencapai fotodegradasi fenol yang tertinggi iaitu 88% disebabkan oleh saiz zarah yang kecil dan juga kandungan nisbah mol titanat yang tinggi di dalam bahan tersebut.

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LIST OF SYMBOLS AND ABBREVIATIONS

FESEM	Field emission scanning electron microscopy
BET	Brunauer-Emmett-Teller
DR UV-Vis	Diffuse reflectance UV-Visible spectroscopy
XRD	X-ray diffraction
ICP-MS	Inductively coupled plasma-mass spectroscopy
CB	Conduction band
VB	Valence band
UV	Ultraviolet light
AC	Alternating current
DC	Direct current
FCC	Face centered cube
nm	Nanometer
Cu K _α	Copper K energy level
mgL ⁻¹	Parts per million
<i>h</i> ⁺	Photogenerated hole
<i>e</i> ⁻	Photogenerated electron
E _g	Band gap energy
eV	Electrovolt
λ	Wavelength
°C	Degree celcius
<i>hν</i>	Energy of photon
μm	Micrometer

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nanomaterials have been an important topic in the field of material chemistry recently. This is due to of its technical and fundamental importance of these materials as they exhibit better properties by looking it in nanoscale. These materials are very useful in manufacturing processes as both industry and laboratory needs this important material. Besides, the development of nanotechnology and nanomaterials will give significant benefits in terms of advantages and improvement to the development of materials [1]. Various types of nanomaterials have been synthesized and discovered by researches due to the high demand in research and development in nanotechnology and improving the state of materials. The nanomaterials structure families with one dimension at least between 1 nm and 100 nm which includes a host of substances such as nanotubes, nanocubes, nanowires, nanoparticles, nanosheets, nanorods and nanobelts. They are very interesting due to their fascinating size dependant optical, mechanical, magnetic, electronic, thermal and chemical properties which are different from their bulk counterparts as well from the molecular or atomic precursors where they were derived. Nanoscale materials promises fascinating properties that are comparable to or superior to those of bulk with point of view of applications in areas ranging from energy storage, fuel cells, nanomedicine, molecular computing, nanophotonics, tunable resonant devices, catalyst and sensing [2].

Nanocrystalline bismuth based materials have been a huge interest for many researchers to the field due to their interesting material properties and application. Bismuth based materials brought great interest in laboratory works and synthesizing it into crystal. Bismuth is a semi metal with a very small band gap which provides a very attractive model system for low dimensional physical phenomena due to its highly anisotropic Fermi surface, low carrier density, small carrier effective masses and long carrier mean free path. Bismuth based materials also have the potential for various application such as ion conductor, in sensor, photocatalyst and many more. Bismuth based materials that have been widely studied are bismuth vanadate (BiVO_4) [3], bismuth germanate (BiGe) [4-5], bismuth phosphate [6], bismuth arsenate [7-8] and bismuth titanate [9-10]. The focus is to synthesize bismuth titanate which is a potential photocatalyst [11].

Other methods such as hydrothermal synthesis, sol gel synthesis and the solid state reaction are the more common methods in synthesizing a bismuth based compounds. These methods has the advantages to synthesize bismuth based materials in a simple way and obtaining single phase crystals but the disadvantages is that they required long hours of synthesis and most of the materials are in micro size. The hot injection gives good quality of nanosize materials compared to other methods.

The hot injection method is relatively new and it has been used in several syntheses. This method was originally used in organic synthesis and lately new discovery and innovations and been found and applied in organometallic field. However, in recent years, this method has been used to synthesize several materials due to its ability of effectively separate nucleation and growth stage [12]. This method has been used to synthesize monodisperse semiconductor nanocrystals. These semiconductor materials which has been successfully synthesize lately are cadmium selenite (CdSe) [13] and indium phosphide (InP) [14].

Previous findings on the hot injection method show that it does not require long hours where it only requires a shorter duration time of few hours. Most importantly, it can produce high quality nanosized crystals via this method [15]. The hot injection method is also considered as environmentally friendly method and it

does not involve dangerous solvents and chemicals bringing it to a whole new height to a greener chemistry approach.

In this research, an attempt had been conducted to synthesize bismuth titanate. Instead of using a common non coordinating organic solvent, the hot injection method was modified by using aqueous solution of nitric acid which is less harmful and allows reaction at lower temperature.

1.2 Problem Statement

The synthesis of bismuth titanate has been one of the most popular topics in environmentally friendly chemistry for the past years on its application as a photocatalyst. However, there are various kinds of method that have been explored to synthesize this compound. Different methods produce bismuth titanate with different morphology, properties and sizes. These several methods that have been used to synthesize bismuth titanate include the solid state reactions, hydrothermal reaction, co-precipitation method, and the sol-gel method. Although this material had been successfully synthesized but none of these methods manage to produce small sizes of nanocrystalline bismuth titanate and lack in homogenized nanosized [16]. So far, these methods had only managed to synthesize in average micro size crystals with inconsistent shape [17]. These methods also consume long reaction duration and preparation of reactants before synthesizing it. Solid state reaction which is commonly used to synthesize bismuth titanate usually gives high agglomeration and compositional inhomogeneity of powders because of high calcination temperature and repeated grinding [15]. Hydrothermal method involves harmful precursors such as titanium sulfate $Ti(SO_4)_2$ while other safer precursors requires autoclave in their methods of synthesizing the compound which is in high temperature and high pressure above atmospheric pressure. On the other hand, the sol-gel method requires long period in synthesizing the compound of at least 12 hours. Limited results are also one of problems using hydrothermal synthesis and the conditions of synthesizing bismuth titanate needs to be optimized [18]. The hydrothermal process is considered a common method of synthesized metal oxides, but it is well known with its

complicated procedures and rigid requirements [18-19]. Others problems occur with this type of synthesis include the usage of expensive precursors and producing non environmentally friendly waste such as harmful solvents and end products [20-21]. There are also not many studies on the growth and structure of bismuth titanate while most of the literatures focus on the photocatalysts activity.

Titanium oxide (TiO_2) is known as one of the most effective photocatalysts for the degradation of organic pollutants and its photocatalytic behavior has been studied broadly. Both liquid and gas phase systems including a wide variety of inorganic and organic pollutant including toxic materials are capable to be decomposed using titanium dioxide. Unfortunately, for large scale applications, their reactivity and selectivity are not enough. Besides, because of the size of its band gap, titanium oxide is effective only under ultraviolet irradiation where λ is less than 380 nm [11]. Sunlight consists of less than 2% ultraviolet light, which means that there is an urgent need to develop new types of photocatalysts responding to visible light irradiation [21]. Generally, there are two approaches that can be explored to develop photocatalysts responsive to visible light irradiation. One of the ways that can be explored is to search for a new material and another one involves the modification of TiO_2 . Asahi and his teammates reported that a TiO_2 catalyst doped with N element absorbed visible light and displayed a higher photocatalytic activity for the decomposition of methylene blue compared to TiO_2 without N doping under visible light irradiation [22]. If a valence band control element is introduced into these materials, it should be a promising photocatalysts with suitable band gaps that responsive to visible light irradiation. Therefore in this project, there is a great interest to evaluate the feasibility of the method in preparing ultraviolet driven photocatalysts using non toxic precursor of TiO_2 . Bismuth titanate is one of the most frequently investigated compounds because of its interesting properties, such as high electrooptical coefficient, low optical activity and high photo sensitivity in the visible region. The compound is also capable to shortened the band gap of TiO_2 hence improving the excitation of electrons in TiO_2 . It also restrains the recombination of electron-hole pairs and increases the photocatalytic activity of TiO_2 [23].

1.3 Objectives of Study

The objectives of the study are:

- i. to synthesize and characterize nanocrystalline bismuth titanate via modified hot injection method.
- ii. to evaluate the photocatalytic performance of the nanocrystalline bismuth titanate.

1.4 Scope of Study

In this research, the modified hot injection method was applied to synthesize the bismuth titanate. The modification was done in the synthesis process where an aqueous solution was used as the solvent instead of non coordinating organic solvent. By modifying the solvent, the reaction temperature can be lowered down to 130°C compared to 240°C if an organic solvent was used. The materials used in this research include the bismuth nitrate, nitric acid, n-n-dimethylformamide, oleic acid and titanium butoxide. In order to characterize the materials, several techniques were used including the X-ray diffraction, Field emission scanning electron microscopy, UV-Vis spectroscopy, N₂ adsorption. In this research, some parameters in synthesis condition were studied to explore the feasibility of the synthesis method. These parameters were heating temperature, ageing time, mole ratio of oleic acid to bismuth and mole ratio of bismuth to titanium. The photocatalytic performance of all the synthesized materials was evaluated through photodegradating phenol under ultraviolet light. Figure 1.1 shows the working hypothesis of synthesis of nanocrystalline bismuth titanate in this project.

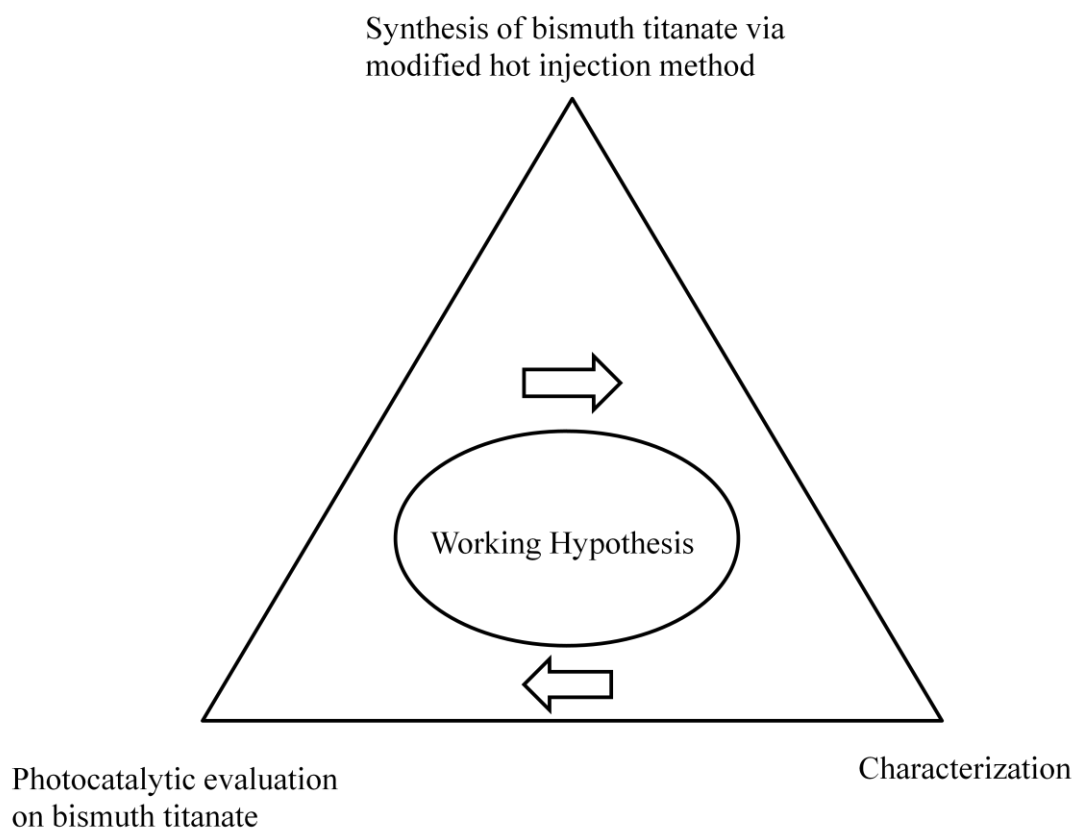


Figure 1.1. The working hypothesis of synthesis of nanocrystalline bismuth titanate.

1.5 Significance of Study

In this work, nanocrystalline bismuth titanate was synthesized through modified hot injection method for the first time. Modification was done on the hot injection method by replacing a normally used non coordination solvent to an aqueous solution. By modifying the solvent, the reaction temperature was reduced almost half of the standard operating temperature, providing a safer synthesis procedure. The effect of synthesis conditions on physico chemical properties of the resulted materials was further explored. The catalytic performance of the synthesized materials in $Fm3m$ and $I23$ space groups was tested through phenol photodegradation under ultraviolet irradiation.

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