EFFECT OF SYNTHESIS PARAMETERS ON STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF NANOCRystALLINE BISMUTH PHOSPHORUS OXIDE MATERIALS

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UNIVERSITI TEKNOLOGI MALAYSIA
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ABSTRACT

Bismuth phosphorus oxide (BPO) has attracted much attention due to its various applications such as catalysts, photocatalysts, ionic conductors, and metal ion sensors. This material is usually produced via solid state reaction, hydrothermal synthesis, and ball milling which are associated with long reaction time, high synthesis temperature, and microsized products. Thus, an attempt was carried out in this research to synthesize nanocrystalline BPO using a relatively simple hot injection method at low reaction temperature. Bismuth acetate and calcium phosphide were used as precursors of bismuth and phosphorus, respectively. Phosphorus precursor reacted with 4 M hydrochloric acid (HCl) to generate phosphine (PH$_3$) gas which later reacted with bismuth precursor in a mixture of 1-octadecene (ODE) and myristic acid (MA). Several parameters in synthesis condition including reaction temperature, type of reaction solvent, ratio of stabilizer (MA) to reaction solvent (ODE), amount of reaction solvent, reaction time, and ageing time were investigated. X-ray diffraction (XRD) results suggested that single phase BPO material with high crystallinity was obtained at reaction temperature 180°C with reaction time of 30 minutes and ratio of MA:ODE of 1:90. The XRD pattern of this material was best fitted with that of reported Bi$_{3.69}$P$_{0.31}$O$_{6.31}$ (PDF 2010:43-0455), implying formation of face centered cubic (FCC) phase with lattice parameter $a = 0.5416$ nm. This FCC phase was in good agreement with transmission electron microscopy (TEM) analysis with average lattice fringes spacing of 0.337 nm. As evidenced, TEM and XRD results showed that particle size of the materials were in range of 10 to 20 nm. These materials are interesting as they have an ordered lamellar structure with both large meso and macro pores, indicating the formation of porous structure between the layers of BPO materials. In conclusion, nanocrystalline BPO was successfully synthesized via hot injection method for the first time.
ABSTRAK

Bismut fosforus oksida (BPO) telah menarik banyak perhatian kerana ia boleh digunakan sebagai pemangkin, foto pemangkin, konduktor ionik, dan pengesan ion logam. Bahan ini biasanya dihasilkan melalui tindak balas keadaan pepejal, sintesis hidroterma, dan kaedah pengisaran bebola yang sering dikaitkan dengan masa tindak balas yang panjang, suhu tindak balas yang tinggi, dan penghasilan produk bersaiz mikro. Oleh itu, suatu usaha telah dijalankan dalam kajian ini untuk mensintesis BPO berhablur nano dengan menggunakan kaedah suntikan panas yang mudah pada suhu tindak balas yang rendah. Bismut asetat dan kalsium fosfida masing-masing telah digunakan sebagai bahan pelopor bismut dan fosforus. Bahan pelopor fosforus telah bertindak balas dengan 4 M asid hidroklorik (HCl) untuk menghasilkan gas fosfin (PH₃) yang kemudiannya bertindak balas dengan bahan pelopor bismut di dalam campuran 1-oktadekena (ODE) dan asid miristik (MA). Beberapa parameter sintesis termasuk suhu tindak balas, jenis pelarut, nisbah penstabil (MA) kepada pelarut (ODE), isipadu pelarut, masa tindak balas, dan masa penuaan telah disiasat. Keputusan pembelauan sinar-X (XRD) mencadangkan BPO berfasa tunggal dengan darjah penghabluran tinggi telah diperoleh pada suhu 180°C dengan masa tindak balas 30 minit dan nisbah MA:ODE bernilai 1:90. Bahan ini sepadan dengan Bi₃.69P₀.₃₁O₆.₃₁ yang telah dilaporkan (PDF 2010:43-0455), mencadangkan pembentukan fasa kiub berpusat muka (FCC) dengan kekisi malar, \(a = 0.5416\) nm. Fasa FCC ini disokong oleh analisis mikroskop penghantaran elektron (TEM) dengan jarak pinggir kekisi berpurata 0.337 nm. Seperti yang dibuktikan, keputusan TEM dan XRD menunjukkan saiz zarah bahan adalah di antara 10 hingga 20 nm. Bahan ini menarik kerana mengandungi struktur lamela yang tersusun dengan liang meso yang besar berserta makro, menunjukkan pembentukan BPO yang berliang. Kesimpulannya, bahan berhablur nano BPO telah berjaya disintesis melalui kaedah suntikan panas untuk kali pertama.
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<tr>
<td>BPO</td>
<td>Bismuth phosphorus oxide</td>
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<tr>
<td>RT</td>
<td>Reaction temperature</td>
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<td>RS</td>
<td>Reaction solvent</td>
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<tr>
<td>RTime</td>
<td>Reaction time</td>
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<tr>
<td>AT</td>
<td>Ageing time</td>
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<tr>
<td>ODE</td>
<td>1-octadecene</td>
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<tr>
<td>HDE</td>
<td>1-hexadecene</td>
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<tr>
<td>TDE</td>
<td>1-tetradecene</td>
</tr>
<tr>
<td>DDE</td>
<td>1-dodecane</td>
</tr>
<tr>
<td>MA</td>
<td>Myristic acid</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<td>FESEM</td>
<td>Field emission scanning</td>
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<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
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<tr>
<td>TEM</td>
<td>Transmission electron</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively couple plasma</td>
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<tr>
<td>PDF</td>
<td>Powder diffractogram file</td>
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<tr>
<td>SAED</td>
<td>Selected area electron</td>
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<tr>
<td>FCC</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>BCC</td>
<td>Body centered cubic</td>
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<tr>
<td>etc.</td>
<td>Et cetera/and other things</td>
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<tr>
<td>e.g.</td>
<td>For example/such as</td>
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<tr>
<td>i.e.</td>
<td>Id est./that is/that is to</td>
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<tr>
<td>h</td>
<td>hour</td>
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<tr>
<td>k</td>
<td>$10^3$</td>
</tr>
<tr>
<td>20</td>
<td>Bragg angle</td>
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<tr>
<td>nm</td>
<td>nanometer</td>
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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Nanotechnology could be defined as an area of engineering of functional systems at a molecular scale. It covers both current works and concepts that are more advanced. Generally, nanotechnology deals with structures of size ranging 1-100 nanometers in at least one dimension. It also involves developing materials or devices within that particular size [1]. Besides, nanotechnology offers diverse research and applications ranging from extensions of conventional device physics to completely new approaches based on molecular self-assembly. In this era, nanotechnology is a rapidly progressing field in pharmaceuticals, sensors, semiconductors, etc. [2]. Recently, the applications of nanotechnology for advanced material, electronic, and medicine fields have been intensively studied to give enormous impact to mankind [2].

Research in nanotechnology for materials science has been focused on morphological features and unique properties at their nanoscale dimensions. One of the interesting topics is functional modifications of materials having not only different structures such as grains, particles, fibres, pores, crystals or other constituent components but also dimensional such as one-, two-, or three-dimension [3-4]. Usually, materials such as carbon nanotubes, zeolites, and metal oxides are having different physical and chemical properties from their bulk counterparts. Most of the nanostructured materials have high potential applications as drug carriers, catalysts, semiconductors, and electronic materials [5]. Moreover, the nanostructured
materials have shown different functions when their structures or dimensions are different from the bulk. For example, the lamellar structure of zinc oxide could extent its surface and interphases in order to retain semiconductor properties of the material [3].

Recently, lamellar nanostructured materials have been widely studied for the development of catalysts, photocatalysts, sensors, solar cells, photoelectrodes, optoelectronics, interconnectors, and nanoscale electronics [3, 6-8]. In general, the lamellar structured materials could be defined as a material with an ordered layered structure e.g. clay, graphite, tungsten disulfide, boron nitride, nickel oxide, and molybdenum sulfides [6, 9-10]. The structure is usually formed by self-assembly of organic surfactant with inorganic species to produce tubes, wires, and sheets structures [3, 6, 11-14]. These different kinds of lamellar structures can also be applied in other potential applications such as separation membranes, drug and gene delivery, etc. [11, 15].

Bismuth-based materials have been intensively investigated for their versatile applications as catalysts, photocatalysts, ionic conductors, metal ion sensors, and separating radioactive elements [16-19]. Up to the past decades, different crystal structures were reported such as monoclinic with monazite-type at low temperature and trigonal at high temperature using hydrothermal synthesis, ball milling synthesis, and chemical vapour deposition (CVD) process [16-20]. These various crystal structures would offer different properties making them useful for different applications. For instance, trigonal bismuth phosphate was used as a catalyst in several reactions [16, 21]. Meanwhile, the monoclinic crystal structure of bismuth phosphate is a potential candidate in ionic conductor field [22-23]. The formation and application of cubic type i.e. face centered cubic (FCC) and body centered cubic (BCC) of bismuth phosphate material, however, were rarely reported.

Nowadays, bismuth-based nanostructured materials have attracted particular attention for their potential applications as catalysts, semiconductors, sensors, optical, and electronic devises [16, 24-25]. The examples of these bismuth based nanostructured materials are bismuth vanadate, bismuth sulphide, bismuth titanate,
bismuth selenide, bismuth ferrite, and bismuth phosphate. In order to further enhance their performances, various types of nanostructured materials have been synthesized such as rods, tubes, plates, spheres, cocoons, flower-likes, and flakes [17-18, 26-27]. They were usually synthesized via solid state reaction, combustion technique, microwave irradiation, co-precipitation, etc. Similarly, nanostructured bismuth phosphorus oxide (BPO) materials have attracted attention due to low band gap that are useful in applications mentioned above [17]. Unfortunately, nanocrystalline BPO could not be obtained through the synthesis methods mentioned above. Moreover, there is no report on formation of nanocrystalline BPO with lamellar structure.

Recently, relatively new and economical method of hot injection has been successfully developed for the synthesis of monodisperse nanocrystals materials such as cadmium selenide (CdSe), cadmium sulphide (CdS), cadmium telluride and indium phosphide (InP) [28-31]. The method was based on injection of cold precursor into a hot solvent, resulting in nucleation burst of nanocrystals in the reaction solvent. It was found that this method has the advantage to separate nucleation and growth stage of synthesized materials, thus particle size of the materials could be easily controlled [30]. In this research, an attempt was carried out to synthesize nanocrystalline BPO materials with lamellar structure via hot injection method. Several parameters in synthesis condition were investigated in order to get the optimum condition for producing high quality nanocrystalline BPO materials.

1.2 Problem Statement

Nanocrystalline BPO material is a potential candidate for catalyst, photocatalyst, ionic conductor, ion sensor, humidity sensor, separating radioactive element, and modifier for electric properties improvement in phosphate glasses. It was reported that the lamellar layered geometry could enhance the effectiveness or efficiencies of the respective applications due to several unique properties e.g. larger surface area and interphases, hence it is challenging to synthesize nanocrystalline BPO with lamellar structure. However, there were limitations of using previous
methods such as inhomogeneous products, long reaction time, and high reaction temperature which subsequently lead to high cost in production. Obviously, the conventional synthesis methods such as hydrothermal synthesis, ball milling, and CVD process are not able to produce materials in lamellar structure.

Therefore, the hot injection method would be used for solving the above problems in order to produce nanocrystalline BPO with lamellar structure since it appears as a promising method in producing nanostructured materials. For this purpose, several parameters in synthesis condition such as reaction temperature, types of reaction solvent, ratio of stabilizer to reaction solvent, amount of reaction solvent, reaction time, and ageing time were investigated to study their effects on the synthesized nanocrystalline BPO materials.

1.3 Objectives of the Study

The objectives of the study were:

a. To synthesize and characterize nanocrystalline BPO materials via hot injection method.

b. To investigate effect of synthesis parameters on structural and morphological properties in producing high quality nanocrystalline BPO materials.

1.4 Scope of the Study

In this research, study was focused on synthesizing BPO nanocrystalline via hot injection method. The possibility to synthesize single phase material with high crystallinity and purity as well as the formation of lamellar structure via this method was explored. In addition, the effectiveness of this hot injection method for preparing good quality nanocrystalline BPO materials was also studied.
Some parameters in synthesis condition were investigated in order to study their effects on the properties of the resulted nanocrystalline BPO materials. These parameters included the reaction temperature, types of reaction solvent, ratio of stabilizer to reaction solvent, amount of reaction solvent, reaction time, and ageing time.

The characterization of synthesized materials was carried out to examine the structural and morphological properties of nanocrystalline BPO materials. In this research, several techniques of characterization were used, including X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX) analysis, surface area and pore size analyses, and inductively coupled plasma-optometry emission spectrometry (ICP-OES).

1.5 Significance of the Study

In this research, the feasibility of synthesizing lamellar structured nanocrystalline BPO materials via hot injection method was investigated. This hot injection method could also be a potential route to prepare good quality nanocrystalline BPO materials in industry scale since this method requires shorter reaction duration and lower reaction temperature.

These BPO materials are potentially applied as semiconductor, ionic conductor, capacitor, catalyst, photocatalyst, separating radioactive elements, ion sensor, thermoelectric devises, etc. It is widely accepted that the performance of these materials could be further increased if they are in their nanoscale having ordered structure which provides them higher surface area and more active sites.
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