

SYNTHESIS OF BISMUTH VANADATE AS VISIBLE-LIGHT PHOTOCATALYST

(Sintesis Bismuth Vanadat Sebagai Fotomangkin Cahaya Nampak)

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Abstract

Bismuth Vanadate (BiVO_4) photocatalyst was synthesized by precipitation methods. Two different sources of bismuth namely bismuth acetate and bismuth nitrate pentahydrate were used. The bismuth solutions were mixed with ammonium metavanadate solution before being titrated against ammonium hydrogen carbonate solution. The precipitate formed using bismuth acetate (B1) was calcined at 450°C and that of bismuth nitrate was calcined at 450°C (B2) and 300°C (B3) under air flow for 4h. The resulting powder were characterized by XRD, FESEM, IR and its surface area. XRD pattern analysis showed that all BiVO_4 sample produced are of monoclinic phase and the FESEM images showed that the particles were agglomerated. The surface area of BiVO_4 produced from bismuth nitrate pentahydrate was higher ($3.9\text{ m}^2/\text{g}$) than that produced from bismuth acetate ($2.7\text{ m}^2/\text{g}$). Photocatalytic activities of the synthesized BiVO_4 were evaluated by photodegrading Methylene Blue dye (MB) under visible light irradiation. The highest photocatalytic activity was observed when using B3 as photocatalyst with percentage removal of 34%.

Keywords: visible light, photocatalyst, bismuth vanadate, methylene blue

Abstrak

Fotomangkin bismut vanadat (BiVO_4) telah disintesis dengan kaedah pemendakan. Dua sumber bismut yang berlainan iaitu bismut asetat dan bismut nitrat pentahidrat telah digunakan. Larutan bismut telah dicampurkan dengan larutan amonium metavanadat sebelum dititrat dengan larutan amonium hidrogen karbonat. Mendakan yang terbentuk menggunakan bismut asetat (B1) telah dikalsin pada 450°C dan yang menggunakan bismut nitrat dikalsin pada 450°C (B2) dan 300°C (B3) dibawah aliran udara selama 4 jam. Serbuk yang terhasil telah dicirikan dengan XRD, FESEM, IR dan luas permukaannya. Analisis pola XRD menunjukkan semua sampel yang terhasil mempunyai fasa monoklinik dan imej FESEM menunjukkan gumpalan partikel. Luas permukaan BiVO_4 yang terhasil daripada bismut nitrat adalah lebih tinggi ($3.9\text{ m}^2/\text{g}$) daripada yang terhasil daripada bismut asetat ($2.7\text{ m}^2/\text{g}$). Aktiviti fotokatalisis bagi BiVO_4 yang disintesis telah dinilai dengan mendegradasi pewarna metilena biru (MB) dibawah radiasi cahaya nampak. Aktiviti fotokatalisis yang tertinggi dapat diperhatikan apabila menggunakan B3 sebagai fotomangkin dengan peratus penyingkiran sebanyak 34%.

Kata kunci: cahaya nampak, fotomangkin, bismut vanadat, metilena biru

Introduction

Recently, environmental contamination has been recognized as one of the greatest problems of modern society, mainly due to the population explosion and the increased industrial activity. Industries, in particular, produce a large amount of effluent containing contaminants which can cause serious environmental problems. Therefore, the removal of these contaminants from industrial wastewater has become a major concern. One of these contaminants is dye. Although many physical, biological or chemical methods have been utilized to treat dye effluents, the use of advanced oxidation process in particular photocatalysis has received great attention in wastewater treatment technology. This is due to its ability to utilize light to photodegrade organic contaminants to harmless products such as CO_2 and water. For the past decades, the most useful photocatalyst is titania (TiO_2) due to its behaviors that are non-toxic, inexpensive, highly oxidative and chemically stable. However due to its large band gap energy (3.2 eV), TiO_2 only respond to UV light irradiation which occupies only 4 % of the whole solar energy [1]. Since 43% of solar light is visible-light, therefore it is necessary to develop photocatalyst which can work in visible light range. Several researchers have used metal to dope TiO_2 which led to the lowering of its band gap energy and shifting its optical response to visible light. Unfortunately, in most cases these dopants also work as a recombination center

between photogenerated electrons and holes, hence reducing the photocatalytic activity of TiO_2 [2]. Thus the development of visible light photocatalyst has become a new challenge to the researchers.

One of the promising non-titania based visible-light driven semiconductor photocatalyst is bismuth vanadate (BiVO_4). It was applied as catalyst in oxidative dehydrogenation of ethyl benzene to styrene [3] and as photocatalyst where O_2 was successfully evolved from aqueous silver nitrate solution under visible-light radiation [4]. There are exactly 3 main crystal forms of BiVO_4 , known as tetragonal (zircon-type structure), tetragonal (scheelite structure) and monoclinic (distorted scheelite structure) [5]. The color of BiVO_4 varies from inhomogeneously yellow-brown to homogeneously lemon yellow depends on many factors including phase composition, stoichiometry, particle size and morphology. The photocatalytic activity of BiVO_4 has also being reported to be strongly influenced by the crystal structure; monoclinic BiVO_4 showed better photoactivity than tetragonal [3].

Several synthesis methods have been used to prepare monoclinic BiVO_4 such as sonochemical method [1], solid-state reaction [5], reflux [6], sol gel [7] and hydrothermal method [8-11]. The photocatalytic activities of BiVO_4 nanocrystals prepared by sonochemical methods, evaluated by decolorization of methyl orange under visible light irradiation, showed better photodegradation rate (95% in 30 min) than that of sample prepared by solid-state reaction (8%) and the TiO_2 (Degussa P25, 6%) under the same conditions [1].

The aims of conducting this work are to study the effect of starting materials and calcination temperatures on the properties of the BiVO_4 photocatalysts prepared by precipitation method. The photocatalytic performance of the photocatalysts will be evaluated by photodegrading methylene blue dye under visible light irradiation.

Experimental

Materials

Bismuth (III) nitrate pentahydrate, bismuth acetate, ammonium metavanadate, nitric acid (70%), ammonium hydrogen carbonate and methylene blue were of laboratory reagent grade and used without purification.

Synthesis of BiVO_4

Samples of BiVO_4 powder were prepared as follow: 0.1M of bismuth acetate solution was mixed with 0.1M of ammonium metavanadate solution and stirred continuously at room temperature until a clear yellow solution was obtained. The solution was titrated with ammonium hydrogen carbonate to induce precipitation. The precipitate formed was filtered and washed several times with distilled water before dried in oven at 60°C overnight. The precursor was grinded and sieved, followed with calcination in air flow for 4 hours at 450°C (B1). Although the same procedures were used to synthesis BiVO_4 using bismuth (III) nitrate pentahydrate as starting material, the bismuth salt was initially dissolved in concentrated HNO_3 prior to mixing with ammonium salt solution. The precipitate obtained was calcined at 450°C (B2) and 300°C (B3).

Characterization

To determine the phase composition of the sample powder, X-Ray Diffraction (XRD) analysis was carried out using Shimadzu XRD-6000 Diffractometer with Nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$), over the 2θ collection range of $20 - 60^\circ$. The morphology of the sample was recorded at 150000 X magnification with 15kV accelerating voltage using Field Emission Scanning Electron Microscopy (JEOL JSM-6700F). The sample was coated with a thin layer of platinum to avoid charging effect and thermal damage during scanning. The FT-IR spectra of the samples, before and after calcination, were recorded in the form of KBr pellets (1% sample) using Perkin-Elmer 1650 Fourier Transform-Infra red Spectrophotometer in the wavenumber range of $4000 - 400 \text{ cm}^{-1}$. Specific surface area of the samples was measured by N_2 gas adsorption at -196°C using Quantachrome AS1Win-Automated Gas Sorption Data instrument.

Photocatalytic activity

The photodegradation efficiency of B1, B2 and B3 were evaluated by photodegrading methylene blue (MB) dye under visible-light radiation. A 0.6g of the catalyst was suspended in MB solution (10 ppm, 1L) in a batch type photoreactor (Figure 1). Air was bubbled into the reaction medium by means of an aquarium air pump to maintain the saturation of the solution with oxygen during the course of reaction. The solution was equilibrated for 10 min in

the dark. Subsequently, the solution was irradiated by a 23W cool day light bulb (Phillips) for 4h. At fixed time intervals, 10mL of the solution taken out and filtered through cellulose nitrate filter (0.45 μ m) to remove the catalyst particles. The concentration of the dye in the test sample was determined by Shimadzu UV-1650PC UV-Visible Spectrophotometer.

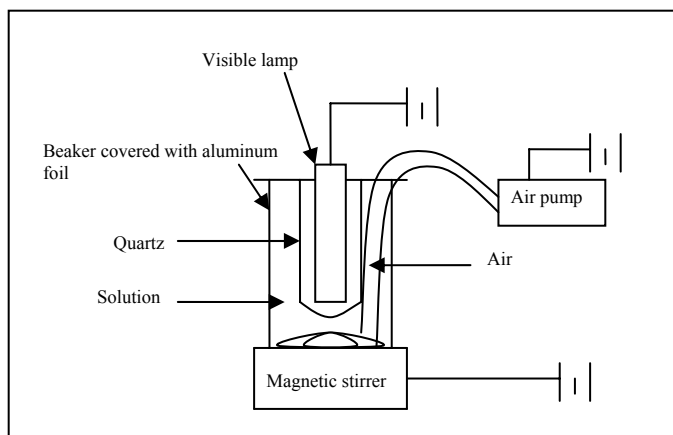


Fig. 1 Schematic set up of the photocatalytic experiments

Results and discussion

X-ray Diffraction analysis

To investigate the phase structure of BiVO₄ powders prepared with different source of Bi and different calcination temperature, the XRD patterns of the prepared BiVO₄ recorded. The XRD patterns are shown in Figure 2. The XRD pattern for all samples, regardless of Bi source and calcination temperature, matched with the JCPDS data no: 14-688 (space group: I2/a, unit cell parameters: a = 5.195Å, b = 11.701Å and c = 5.092Å) which correspond to monoclinic phase of BiVO₄. According to Yu et al. (2009) [12], the crystal structure of monoclinic scheelite BiVO₄ is much similar to that of tetragonal scheelite, except for the distortion. The Bi-O polyhedron in the former is more distorted than that of tetragonal due to the presence of a 6s² lone pair of Bi³⁺. In XRD patterns, these distinctive differences can be reflected by that monoclinic scheelite BiVO₄ generally shows a peak at 15° and well splitting of peaks at 18.5°, 35.0° and 46° of 2 θ . It was observed that none of the synthesized BiVO₄ has a peak at 2 θ = 15°. However, except for B1, the peaks observed at 2 θ = 18.5°, 35.0° and 46° are not well splitted for sample B2 and B3. These phenomena suggested that the structures of the precipitated samples of B2 and B3 are of monoclinic scheelite type, but with less distortion.

Fourier Transformed-Infra Red (FT-IR)

The FT-IR spectra of all BiVO₄ samples before and after calcination are shown in Figure 3. A broad band at 3440.00 cm⁻¹ and a small band at 1624-1630 cm⁻¹ were observed for uncalcined samples and were assigned to O-H stretching and O-H bending mode, respectively. The band around 730 – 1000 cm⁻¹ was attributed to the ν_3 antisymmetric stretching mode of VO₃⁴⁻. The peak observed at 1392 cm⁻¹ (B1) and 1386 cm⁻¹ (B2, B3) was assigned to stretching mode of acetate (COO) and NO₃ groups, respectively. After calcination, only the broad band around 600-800 cm⁻¹ due to V-O stretching mode was observed. This peak was in agreement with previous literature reports [10]. The disappearance of the peaks attributed to acetate and nitrate groups indicates that the calcination temperature used is sufficient for the transformation of the precursors to BiVO₄.

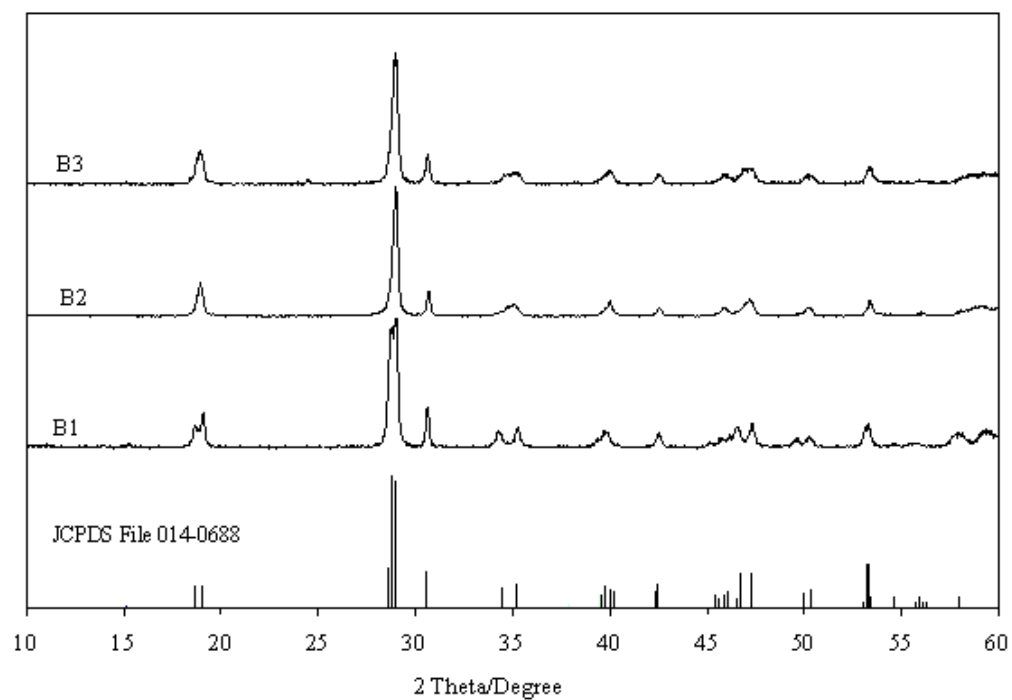


Fig. 2: X-Ray Diffraction patterns of the (a) B1, (b) B2 and (c) B3

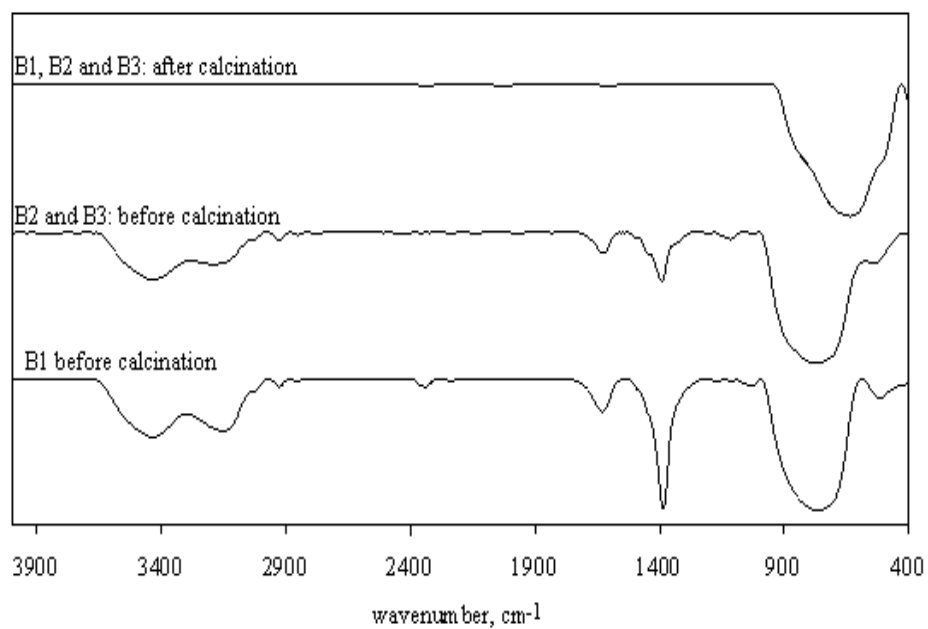


Fig. 3: FT-IR spectra of the BiVO₄ precursor and BiVO₄ after calcination

Field Emission Scanning Electron Microscopy (FE-SEM)

The FESEM micrographs of the prepared BiVO_4 (Figure 4) showed that the morphology of the samples are the same, spherical shape particles agglomerated to form bigger particles. At low temperature, the agglomerated particles formed a flake like structure (B3) but formed irregular spherical structure when calcined at 450°C . This shows that the morphology of BiVO_4 is influenced by the calcination temperature.

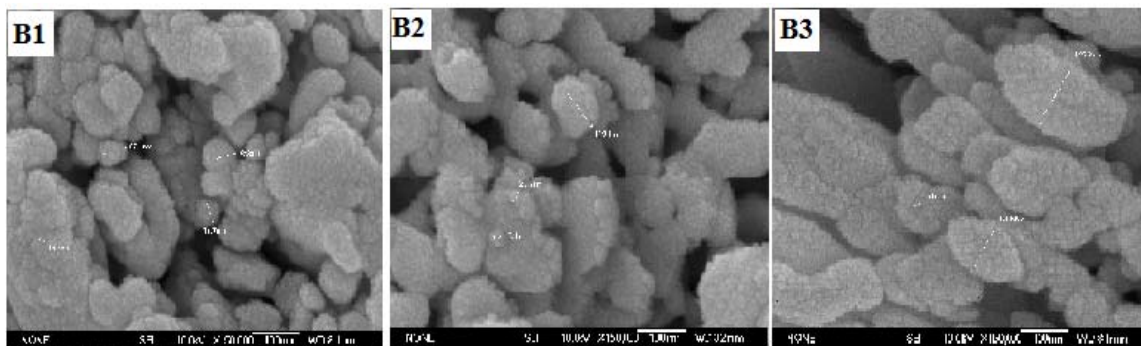


Fig. 4: FE-SEM images on the morphology of the prepared BiVO_4

Surface Area Measurement

The surface area of BiVO_4 samples was determined using N_2 adsorption data. The surface area for B1, B2 and B3 was 2.7, 3.9 and $4.3 \text{ m}^2/\text{g}$ respectively. The highest surface area observed for B3 can be due to calcinations process where the sample was calcined at much lower calcination temperature. All prepared samples however possessed higher surface area compared to BiVO_4 synthesized via solid state reaction, which is $0.26 \text{ m}^2/\text{g}$ [1].

Photocatalytic activity of bismuth vanadate

The photocatalytic activities of B1, B2 and B3 were evaluated by degrading Methylene Blue (MB) dye solution under visible light irradiation. A 23W light bulb was used as a visible light source and the experiments were carried out at room temperature for 4 h. Prior to photocatalysis experiment, the amount of MB dye removed via photolysis and adsorption process was determined. 11 % of the dye was removed via photolysis after 4h of irradiation time.

The removal of MB over different BiVO_4 samples was illustrated in Figure 5. The results showed that the percentage removal of MB by B1, B2 and B3 in absence of light (adsorption) was low, which were 2.2, 14.0 and 18.5%, respectively. However, under visible light irradiation, significant increase in the percentage removal of MB was observed. Even though higher percentage of MB photodegraded by BiVO_4 has been reported, the authors have used a much higher intensity of light (200 watt of Xe arc lamp) [12] compared to this studies (23 watt). This indicates the potential of the prepared BiVO_4 to be used as photocatalyst in photodegrading MB dye at low light intensity.

The high photocatalytic activity of B3 is attributed to two processes: adsorption of MB on the surface of the catalyst and the photodegradation by the catalyst. As B3 posses the highest surface area, it is expected that more active sites are available for the adsorption of MB molecules and adsorption of visible light irradiation to induce the photocatalytic reaction. Interesting for B1, a significant enhancement in the MB removal via photocatalysis was observed. This may be due to the difference in crystal structure of B1 compared to B2 and B3. Although all samples have the monoclinic scheelite phase, B1 has higher distortion than B2 and B3 as illustrated from XRD analysis.

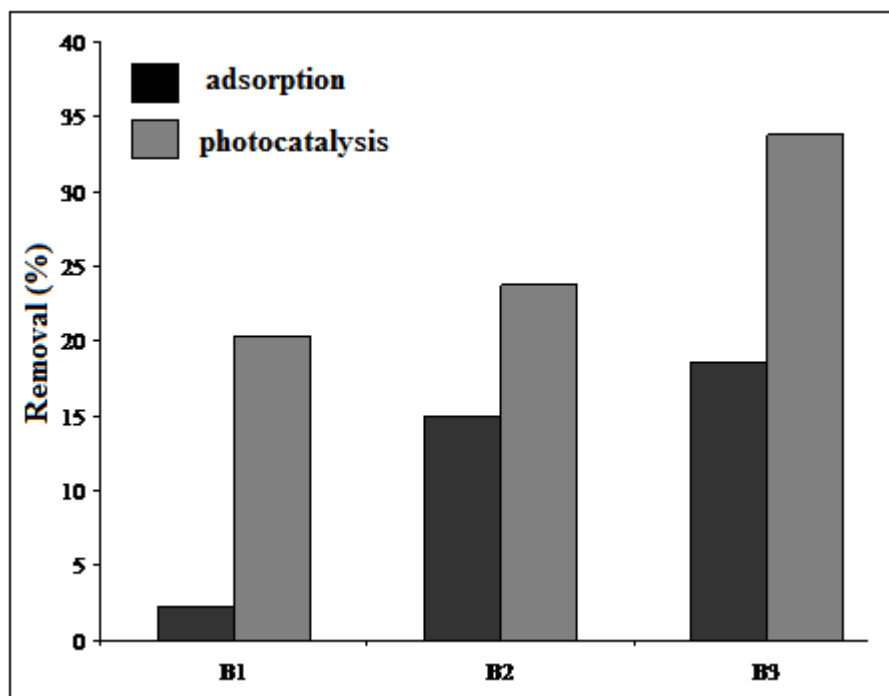


Fig. 5: The removal of MB via adsorption and photocatalysis process by BiVO_4 catalysts. Condition: Mass of BiVO_4 = 0.6 g, Concentration of MB = 10ppm

Conclusion

BiVO_4 has been successfully synthesized through precipitation method. A more distorted monoclinic scheelite type BiVO_4 was obtained when using bismuth acetate as starting material. The morphology of the agglomerated particles is influenced by calcinations temperature where flake like structure is observed at low temperature and irregular spherical shape at high temperature. The removal of MB dye by BiVO_4 is influenced by surface area and the crystal structure of the catalyst. The higher the surface area of the catalyst, the higher the removal by adsorption process. Removal of MB via photocatalytic processes is more dominant than adsorption process for a more distorted monoclinic scheelite BiVO_4 .

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