A Facile Synthesis and Properties of Bismuth Vanadate (BiVO$_4$) Photocatalyst by Hydrothermal Method

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Abstract. In this study, BiVO₄ photocatalysts were synthesized by hydrothermal method using Bi(NO₃)₃.5H₂O and NH₄VO₃ as raw materials followed by calcination at different temperatures in the range from 350 ^{o}C to 600 ^{o}C. The as-synthesized BiVO₄ samples were characterized by a number of physicochemical techniques including X-ray diffraction (XRD), Raman analysis, Scanning Electron Microscopy (SEM), and UV-Visible (UV-Vis) light diffuse reflectance spectrophotometry. The effect of temperatures calcination on structure, surface morphology, visible-light photocatalytic activity and light absorption performance of BiVO₄ was discussed in details.

1. Introduction

In chemistry, the traditional photocatalysts comprise mainly metal oxides such as TiO₂, ZnO, SnO₂ and CeO₂. These photocatalysts are semiconductors with relatively low band-gap and are therefore suitable for absorbing natural or artificial light and exhibiting photochemical activity [1-10]. Optical catalysts play an important role in many areas such as environmental improvement, photovoltaic applications, bio-applications, clean energy production, sensors, nanoscale electronic components and solar battery. One of such photocatalysts is the BiVO₄, which has been attracting a lot of attention due to its remarkable features, including low band gap energy, good dispersion, non-toxicity and high photochemical activity under visible light irradiation. Several synthesis methods have been utilized in order to prepare BiVO₄ powder of high quality with predominantly solid-state including aqueous-based and hydrothermal methods [11-15].

In this study, a simple solution-based preparation method under acidic conditions has been selected and adopted, involving the calcination of obtained BiVO₄ precipitates at different temperatures. Subsequently, an in-depth analysis of important physical parameters of as-obtained products allows for a coherent correlation with the different photocatalytic O₂ evolution. The insights gained from this analysis contribute to the better understanding of the visible-light water oxidation mechanisms and more efficient optimization of photocatalytic materials. The objective of this study was to synthesize

$BiVO_4$ materials by hydrothermal method. Following that, the as-synthesized samples were calcined at different temperatures ranging from 350 ^{o}C to 600 ^{o}C. Structural properties of material samples calcined at different calcination temperatures from 350 ^{o}C to 600 ^{o}C were characterized using analytical methods including XRD, SEM and UV-Vis-DRS.
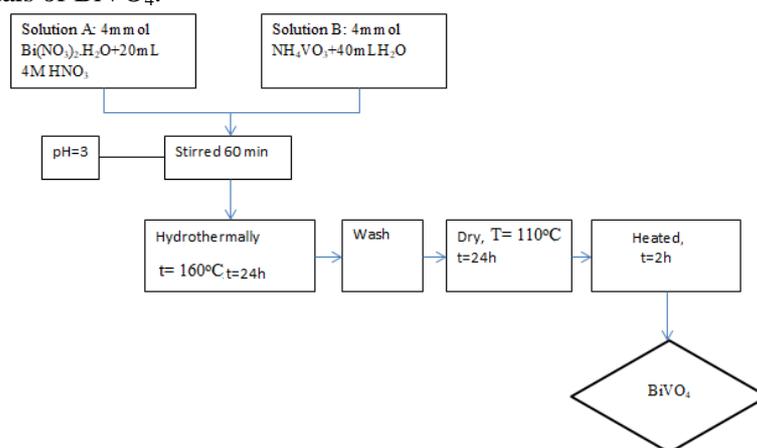
2. Materials and Method

2.1. Materials

Chemicals used in this study include Ammonium metavanadate (NH_4VO_3, $\geq$ 98%, Sigma-Aldrich), Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$, $\geq$ 98.0%, Sigma-Aldrich), Nitric acid (HNO_3, 65-68%), and ammonia solution (NH_4OH 25-28%, Xilong). Chemicals for analysis: Rhodamine B (RhB, Jihuada), Distilled water (from Lasany's two-storey water machine).

2.2. Synthesis of $BiVO_4$ photocatalyst by hydrothermal method

The typical preparation process comprises six-step as follows: (1) 4 mmol of $Bi(NO3)_3.5H_2O$ was dissolved in 20 mL of 4M HNO_3 solution; (2) another solution was prepared by dissolving a stoichiometric of NH_4VO_3 in 40 mL of hot water; (3) The two solution was mixed together and stirred for about 1 hour to achieve a stable and homogeneous state; (4) The pH of the mixture is adjusted with NH_4OH or HNO_3 solution; (5) The mixture was sealed in an autoclave, and subjected to heat at 160 ^{o}C for 24 hour under pressure. At the end of the process, the precipitate was filtered, washed with distilled water and dried overnight at 110 ℃; (6) The obtained solid was calcined in air at different temperature (350 ^{o}C, 400 ^{o}C, 450 ^{o}C, 500 ^{o}C and 600 ^{o}C) for 2 hour. To investigate the effects of calcination temperature on the formation of crystalline and phase structure of $BiVO_4$, $BiVO_4$ samples synthesized by hydrothermal method were calcined at different temperature (350 – 600 ^{o}C) to analyze the structural crystals of $BiVO_4$.

Scheme 1. Process of synthesis of materials by hydrothermal method.

In this study, $BiVO_4$ was synthesized by hydrothermal followed by calcination process at different temperatures (from 350 ℃ to 600 ℃) as shown in Table 1.

Table 1: *Statistical samples and aggregate conditions*

Calcinated Sample	Heat (^{o}C)	Time (h)	Sample characteristics	Efficiency (g)
BVO-350 ^{o}C	350 ^{o}C	2	Yellow powder	83%
BVO-400 ^{o}C	400 ^{o}C	2	Yellow powder	90%
BVO-450 ^{o}C	450 ^{o}C	2	Yellow powder	81%
BVO-500 ^{o}C	500 ^{o}C	2	Yellow powder	83%
BVO-600 ^{o}C	600 ^{o}C	2	Yellow powder	78%

2.3. Characterization

Samples were analyzed on Jeol JSM 7401F Scanning Electron Microscope instrument, at the Institute of Chemistry, Vietnamese Academy of Science and Technology. X-ray diffraction (XRD) powder analysis was carried out with a Rigaku D/max-RB12KW X-ray diffractometer using Cu K_α radiation (λ = 1.5418 Å) in the 2θ range of 4–80° at room temperature. The XRD was developed by William L.Bragg in 1913, in which the Bragg equation (1) is considered as a condition for diffraction: $d =$

$\frac{n\lambda}{2sin\theta}$, where λ is the X-ray wavelength (1.5418Å). The diffraction angle θ corresponds to the diffraction peaks on the diffraction pattern defined θ = arcsin ($n\lambda$ / 2dhkl), n, or diffraction patterns, takes the values of 1, 2 or 3 .

3. Results and Discussion

The crystalline structure of $BiVO_4$ was confirmed by XRD patterns as shown in the Figure 1. The results showed that all samples had strong diffraction peaks at 28° and 30.6^o, and split diffraction peaks at 18.5^o, 34°, and 46°. This result corresponds to the standard of the $BiVO_4$ crystalline monoclinic scheelite crystal (m-$BiVO_4$, JCPDS card no. 14-00688) and is consistent with previous studies [15]. In addition, all samples show the characteristic peak splitting diffractions at 2θ = 18.5, 34 and 46° [16]. Even though monoclinic phase was observed at every calcination temperature, splitting of the these characteristic peaks becomes more pronounced as the calcination temperature increases, which likely signifies the increasing crystallinity degree of the (s-m) phase in $BiVO_4$ samples [16,17].
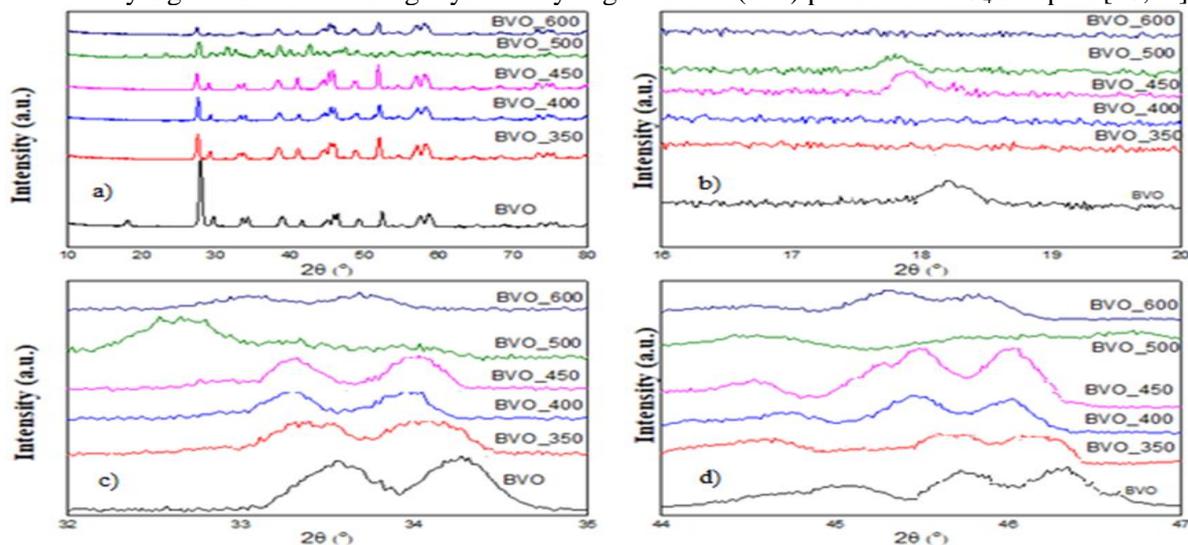

Figure 1. a) XRD diagram of $BiVO_4$ samples, b) XRD is at 2 °from 16° to 20°, c) The XRD detail diagram at 2θ from 33° to 34.5^o, d) The XRD detail diagram 2θ from 44° to 47°.

Crystal shape, particle size and particle distribution of the material were observed through SEM images which are given in the Figure 2. Visually, materials and structures have flattened shape which is 1 μm in size and is 1 μm in flange size. At calcination temperatures of 450 ^{o}C, , the form of the materials is spherical and rod-shaped.
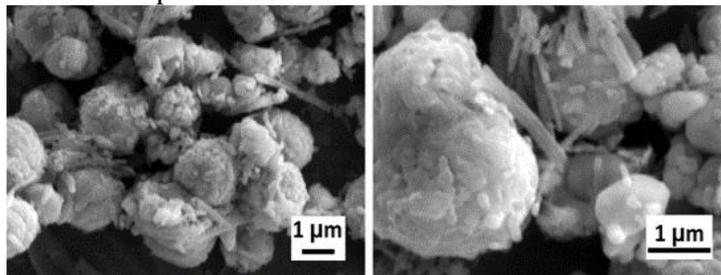

Figure 2. SEM images of the samples $BiVO_4$ in: BVO-450°C.

The vibrational properties of the $BiVO_4$ crystals were studied through Raman scattering spectrum at room temperature as shown in the Figure 3. The results show that the samples exhibited specific vibration levels for the m-s crystalline $BiVO_4$ and the thermal increases through the hydrothermal method, the intensity of these oscillations decreases, affecting the crystalline structure of the material. In the Figure 3, Raman spectra of $BiVO_4$ powders were excited by a red (648 nm) laser and corresponding spectra. Raman spectroscopy can provide structural information and is also a sensitive method for the investigation of the crystallization, local structure, and electronic properties of materials. Raman bands at around 210, 324, 366, 640, 710, and 826 cm^{-1} were observed for all samples. These are the typical vibrational bands of $BiVO_4$ [15,18]. The structural information of

$BiVO_4$ is given by the band centered at 210 cm^{-1}. The asymmetric and symmetric formations of VO_4 tetrahedron are given by the bands centered at 324 and 366 cm^{-1}, respectively. The Raman band at 640 cm^{-1} can be assigned to the asymmetric stretching vibration of the shorter V-O bond. The stretching modes of two vibrational modes of V–O bonds are determined by the bands centered at 710 and 826 cm^{-1}. These two bands provide valuable information about the structural variations among the powder samples calcined at different temperatures. It has been observed a positive shift in the vibrational mode of V-O, which varies from 825.30 to 827.52 cm^{-1}. The Raman stretching frequencies and the respective metal-oxygen bond lengths share an inverse relationship which describes that a higher stretching frequency will correspond to a lower metal-oxygen bond length. By utilizing the expression for bond length [18,19]: $V(cm^{-1}) = 21349 \exp(-1.9176 R(^{o}A))$ (2), where V is the stretching Raman frequency for V–O, it can be seen that the bond length varies from 1.6964 ^{o}A to 1.6950 ^{o}A for 350 ^{o}C and 600 ^{o}C sample, respectively [20].
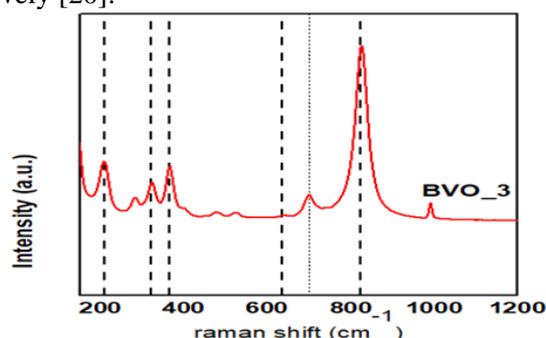

Figure 3. Location of the sample Raman scattering spectrum

The photocatalytic performance of samples was strongly associated with the optical absorption property. Therefore, UV-vis diffuse reflectance spectra (DRS) was utilized to further investigate the absorption band the band gap energy values of the crystals. It can be seen from Figure 4 that all of the five samples showed absorption bands in the visible light region, and the absorption edges of the samples exhibit a slight red shift when the Bi is present. The optical band gap energies of the five samples were estimated from the absorption spectra by using the following relationship: $\alpha h\nu = A(h\nu - Eg)^{n/2}$ where α, $h\nu$, A and Eg are the absorption coefficient, the photon energy, constant, and the optical band gap energy, respectively. The value of n depends on whether the transition is direct (n = 1) or indirect (n = 4), and it was determined to be unity on the absorption spectra. The band gap energy was determined by extrapolating the linear part of $(\alpha h\nu)^2$ vs. $h\nu$ plot of the energy axis as showed in Figure 4. The 2.42 eV value for pure m-$BiVO_4$ is in agreement with the literature [21].
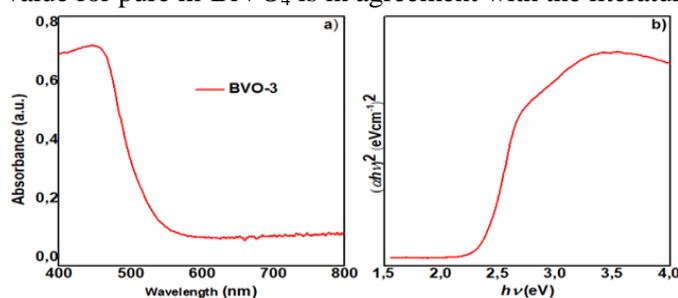

Figure 4. UV-vis diffuse reflectance spectra (DRS) of $BiVO_4$ and Plot of the transformed Kubelka–Munk functions vs. the energy of light.

4. Conclusion

In this study, $BiVO_4$ photocatalyst was synthesized by a simple hydrothermal followed by calcination process at different temperatures (350 ^{o}C, 400 ^{o}C, 450 ^{o}C, 500 ^{o}C, 600 ^{o}C). The structure of materials were evaluated by chemical and physical methods such as XRD and SEM modern. The results indicate that the calcining at different temperature affects the formation of the crystal form of $BiVO_4$. UV-vis diffuse reflectance spectra (DRS) was utilized to further investigate the absorption band the band gap energy values of the $BiVO_4$ crystals

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