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Synthesis, Characterization, and Photocatalytic properties of $BiVO_4$ particles prepared by a co-precipitation process

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Abstract

The Bismuth vanadate ($BiVO_4$) particles were prepared by co-precipitation method from Bismuth (III) nitrate as starting precursors and nitric acid (HNO_3) was selected as the solvent. The as-precipitated particles were calcinated at 200 °C, 300 °C, 400 °C, and 500 °C for 8 h. The influence of different calcination temperatures on structural, morphological, and photocatalytic properties of all samples was studied. The crystal structures were investigated by X-ray diffraction (XRD) and surface morphologies were observed by scanning electron microscope (SEM). The XRD results show the phases change of Tetragonal to Monoclinic and the SEM images show uniform structure with the significant agglomeration of $BiVO_4$ particles when calcination temperature increases. Moreover, Photocatalytic testing was studied by decomposition of RhB dye solution with $BiVO_4$ particles prepared at different calcination temperatures under visible light irradiation and the result exhibited that the product calcined at 400 °C performed better activity than the others that would be due to the existence of mixed phases of $BiVO_4$ and high surface area.

Keywords: Bismuth vanadate ($BiVO_4$), Photocatalyst, co-precipitation process

1. Introduction

In recent years, $BiVO_4$ is considered as a potential visible-light-driven photocatalyst for the extensive application of solar energy harvesting. $BiVO_4$ has attracted significant interest regarding its considerable properties such as good dispersibility, non-toxicity, and good photocatalytic result in degradation under visible-light illumination with a suitable optical band gap of 2.4-2.8 eV, depending on its crystalline phase [1-2]. Many reports have recently focused on the effort to adjust crucial properties of $BiVO_4$ by vary pH, precursor concentration, or calcination temperature [3]. Moreover, there are three main crystalline phases of $BiVO_4$ with monoclinic(s-m) phase, tetragonal(s-t) phases and tetragonal zircon (z-t) [4-6] that can be modified by synthesis processes and processing conditions. Hence, the calcination temperature is one of the important parameters of the precipitation process that is always required to obtain a uniform and well-defined structure of the products. Furthermore, the photocatalytic reaction is considered as an effective route of treatment for the decomposition of toxic composition to final non-toxic compounds. Based on the literature, there are various synthesis processes employed for preparing $BiVO_4$-based materials including the sonochemical process [7], sol-gel method [8], hydrothermal process [9], and co-precipitation method [10]. Among these processes, the co-precipitation process is among practical processes for nanoparticle synthesis since it is an economical and facile process for

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large scale production and the product quality can be controlled and adjusted by process conditions and parameters such as starting precursor, doping precursor, and post-heat treatment.

In this work, we report the extensive characterization of crystal structure, morphology, optical property, and photocatalytic performance of co-precipitated bismuth vanadate ($BiVO_4$) particles calcined at moderate temperatures up to 500 °C.

2. Experimental details

Chemicals with analytical grade were used for starting precursors. Bismuth nitrate pentahydrate ($Bi(NO_3)_3 \bullet 5H_2O$) was used as bismuth source and ammonium metavanadate (NH_4VO_3) selected for vanadium source was purchased from Ajax Finechem Laboratory Chemicals company. The couple chemicals solution of nitric acid (HNO_3) as solvent and ammonium (NH_3) for pH adjustment were collected from Univar Ajax Finechem company. The bismuth vanadate ($BiVO_4$) particles were synthesized via the co-precipitation method. First of all, 0.012 mol of $Bi(NO_3)_3 \bullet 5H_2O$ was dissolved in 50 ml of 2 M HNO_3 solution while NH_4VO_3 was separately dissolved in the same solvent. The precursor solution was continuously stirred at room temperature for 10 minutes to obtain the clear solution. After that, both prepared solutions were together mixed under continuous stirring at room temperature then pH value of the mixed solution was adjusted by dropwise of NH_3 until the pH of the solution became neutral and was kept stirring at room temperature for 2 h to obtain the yellow suspension. Finally, the suspension was filtered and washed with DI water for 3 times and dried at 100 °C in an oven overnight to appear in fine yellow powder. The as-prepared powder was calcined for 8 hours at various temperatures of 200 °C, 300 °C, 400 °C, and 500 °C. The relevant properties of $BiVO_4$ were investigated by several techniques. The crystalline structure of the synthesized product was probed by X-rays diffraction technique (Rigaku: SmartLab). The morphological property of the prepared particles was observed by scanning electron microscope (Thermo Scientific Apreo S). The photocatalytic performance of the co-precipitated $BiVO_4$ particles was studied by photodecomposition of Rhodamine B (RhB) dye solution using as organic compound under visible light (Philip LED strip cool light 5W) irradiation as a light source.

3. Results and discussion

The crystallinity of the co-precipitated bismuth vanadate ($BiVO_4$) particles calcined at different temperatures was investigated by X-ray diffraction technique as shown in Fig. 1. The prominent peaks observed at 24.5° and 32.7° typically correspond to (200) and (112) crystal planes (square) of the tetragonal zircon $BiVO_4$ (t-$BiVO_4$) (JCPDS No: 14-0133). Correspondingly, the monoclinic $BiVO_4$ (m-$BiVO_4$) shows the characteristic diffraction peaks at 28.9° and 31.2°, corresponding to (121) and (040) crystal planes (circle) (JCPDS No: 14-0688) [11]. For the as-prepared sample and the samples calcined at 200 °C, 300 °C, 400 °C, the mixed phases of tetragonal and monoclinic phases are observed. This result well coincides with the result reported in previously published work conducted by B. Baral and colleague [12] who reported the existence of monoclinic and tetragonal mixed phases of co-precipitated $BiVO_4$ (MT-$BiVO_4$) as the samples were calcined at 400-500 °C, thereafter its crystal structure completely became monoclinic phase at a calcined temperature of 600 °C.

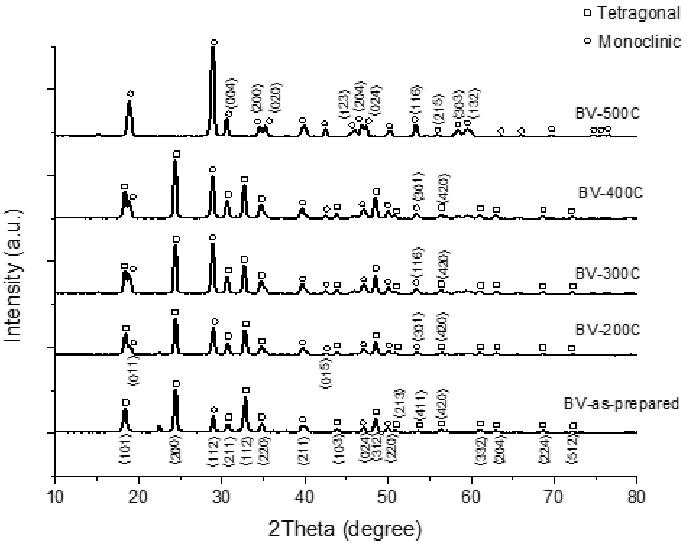

Fig. 1. The XRD patterns of the ZrN thin films, prepared at different operating pressures.

In this work, the phase transformation from tetragonal to complete monoclinic phase of co-precipitated $BiVO_4$ without any presence of impurity phases is observed at a calcination temperature of 500 °C that is lower than the report by B. Baral *et al.* [12]. Typically, MT phase transformation of $BiVO_4$ is correlated to the activation energy provided during the calcination process for inhibiting the crystal growth of the tetragonal phase by the increasing of the growth of the monoclinic phase. This specific phase-change temperature could be varied due to the preparing condition of the precursor of the co-precipitation process and calcination environment.

The crystallite size of $BiVO_4$ particles can be calculated from the full width at half maximum of the (112) diffraction peak of the $BiVO_4$ monoclinic structure by Scherrer's formula.

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

Where D is the crystallite size, K is the shape factor, λ is the X-ray wavelength of $CuK\alpha$, β is the full width at half maximum (FWHM) and θ is the Bragg angle. The calculated crystallite sizes of $BiVO_4$ particles are shown in Fig. 2. The average crystallite size of $BiVO_4$ particles increases from 150 nm to 185 nm as the calcination temperature increases from 200 °C to 500 °C. This feature indicates that the crystallinity of the particles significantly improves with increasing post-treated temperature.

Fig. 3 shows the surface morphologies of as-prepared $BiVO_4$ particles and $BiVO_4$ particles calcined at different temperatures of 200-500 °C. At a calcined temperature range of 200 °C-400 °C, it is observed that the size of the calcined samples is approximately 500 nm -800 nm and their size tends to increase with increasing temperature. Moreover, as clearly seen in SEM images of the samples calcined at 300-400 °C, there are two different structures with the difference in their size, which could reflect the mixture of two phases of $BiVO_4$ as supported by XRD results. As calcination temperature is elevated to 500 °C, the corresponding image shows a uniform structure with significant agglomeration to form a cluster of $BiVO_4$ particles.

The SEM results accompanying XRD results suggest that the calcination temperature is a crucial synthesis factor playing a key role in the crystal structure, phase transformation, and morphology of $BiVO_4$ prepared by the co-precipitation process.

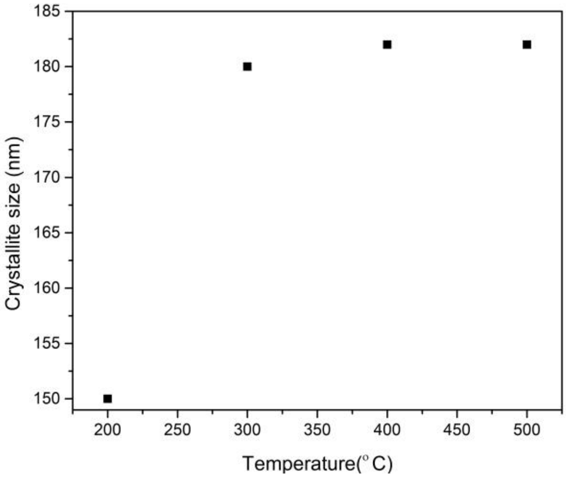

Fig. 2. The calculated crystallite size of $BiVO_4$ particles calcined at 200-500 °C.

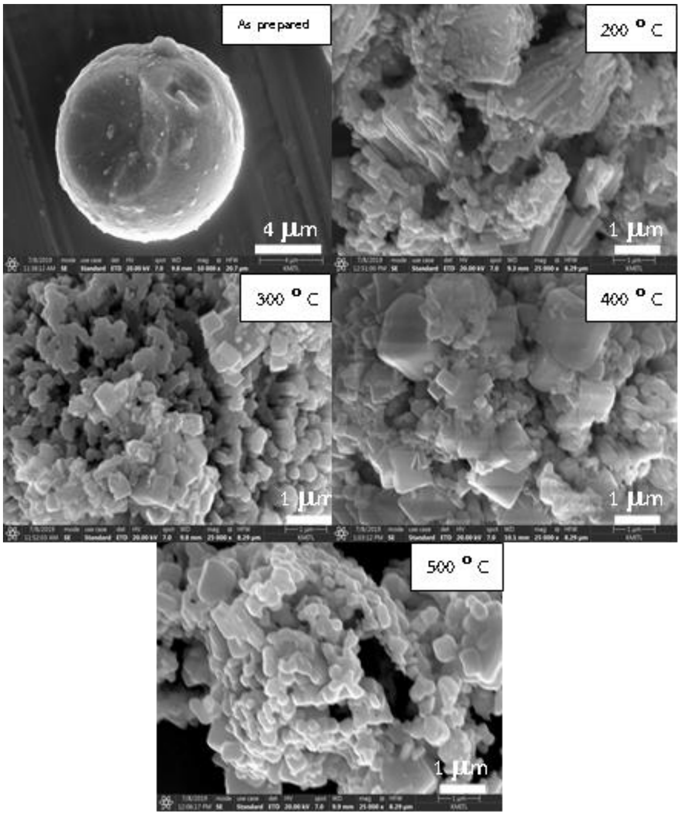

Fig. 3. SEM micrographs of as-prepared $BiVO_4$ particles and $BiVO_4$ calcined at 200-500 °C.

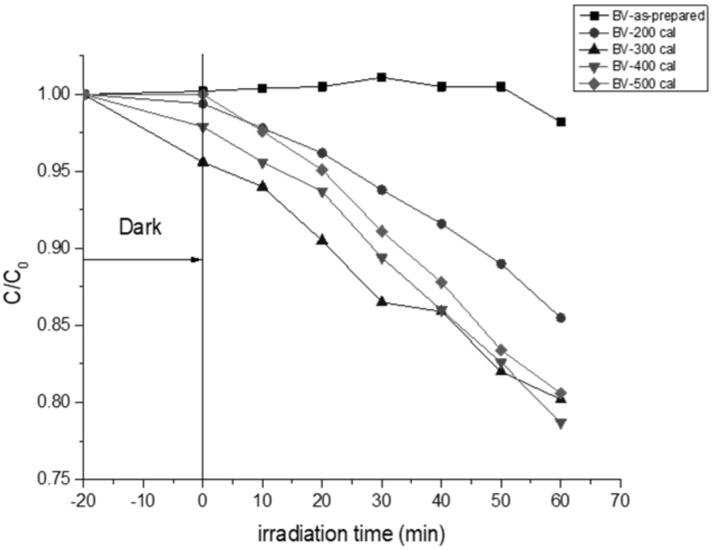

Fig. 4. Photocatalytic of as-prepared $BiVO_4$ particles and $BiVO_4$ calcined at 200 °C-500 °C under visible light irradiation.

Fig. 4 shows photocatalytic testing for the decomposition of RhB dye solution with $BiVO_4$ particles prepared at different calcination temperatures under visible light irradiation. Before irradiation, a slight decrease in dye concentration can be observed that is due to the self-adsorption of the catalysts. During visible irradiation, all samples except the as-prepared product exhibit a good reaction of dye degradation accompanying the significant decrease in dye concentration with increasing reaction time.

The general principles of a photocatalyst undergo oxidation process and reduction process in attendance of light energy. The main reactions that take place during photocatalysis are proposed as below reactions (2)-(5).

$$Photocatalysts \xrightarrow{hv} e^-_{CB} + h^+_{VB} \tag{2}$$

$$Photocatalyst \ (e^-_{CB}) \longrightarrow O_2 + O_{2\cdot-} \tag{3}$$

$$Photocatalyst \ (h^+_{VB}) \longrightarrow H^+ + \bullet OH \tag{4}$$

$$Pollutants + \bullet OH + \ O_{2\cdot-} \longrightarrow Degradation\ products \tag{5}$$

In the case of the as-prepared sample, less photocatalytic performance is noticed that could be due to the less active surface area of the product as observed by SEM. Among the others, the sample calcined at 400 °C performed superior photocatalytic activity under visible irradiation. This result could be attributed to the greater surface area and a higher degree of crystallinity of the product calcined at this certain temperature. The other reason could be ascribed to the mixed MT-phase of the product when it was calcined at this temperature. This mixture of these two phases will probably form the compatible and well-matched heterojunction at their interfaces that can effectively retard the photogenerated electron-hole recombination process and consequently significantly enhance its catalytic performance [12].

4. Conclusion

In summary, $BiVO_4$ particles were prepared by the co-precipitation method along with calcination at the temperature range of 200-500 °C. The results of XRD and SEM suggested that the well-defined $BiVO_4$ particles could be obtained by the assistance of calcination at moderate temperatures. The calcination temperature is an important factor having a significant effect on the crystallization, morphology, and phase transformation from tetragonal to the monoclinic phase of $BiVO_4$ at a certain temperature range of 400-500 °C. The good photocatalytic activity of catalyst under visible irradiation was performed by $BiVO_4$ particles calcined at 400 °C regarding the appearance of mixture tetragonal-monoclinic phase with higher active surface area and formation of well-matched heterojunction at their interfaces effectively prolong the recombination time of the photo-generation electron-hole pair during the photocatalytic reaction.

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References

[1] Osmando FL, Kele CTG, Gabriel KM, Vagner DMR, Waldir JrA, Caue R. Synthesis of $BiVO_4$ via oxidant peroxo-method: insights into the photocatalytic performance and degradation mechanism of pollutants. New J. Chem. 2015;39:6231-7.

[2] Venkatesan R, Velumani S, Kassiba A, Mechanochemical synthesis of nanostructured $BiVO_4$ and investigations of related features. Mater. Chem. Phys. 2012;135:842-8.

[3] Yu J, Zhang Y, Kudo A. Synthesis and photocatalytic performances of $BiVO_4$ by ammonia co-precipitation process. J. Solid State Chem. 2009;182:223-8.

[4] Ravidhas C, Juliat JA, Sudhagar P, Devadoss A, Terashima C, Nakata K, et al. Facile synthesis of nanostructured monoclinic bismuth vanadate by a co-precipitation method: Structural, Optical and Photocatalytic properties. Mater. Sci. Semicond. Process. 2015;30:343-51.

[5] Huo R, Yang XL, Liu YQ, Xu YH. Visible-light photocatalytic degradation of glyphosate over $BiVO_4$ prepared by different co-precipitation methods. Mater. Res. Bull. 2017;88:56-61.

[6] Malathi A, Madhavan J, Ashokkumar M, Arunachalam P. A review on $BiVO_4$ photocatalyst: Activity enhancement methods for solar photocatalytic applications. Appl. Catal., A 2018;555:47-74.

[7] Mason TJ, Lorimer JP. The uses of power ultrasound in chemistry and processing. J. Chem. Technol. Biotechnol. 2002;79:303.

[8] Pookmanee P, Kojinok S, Puntharod R, Sangsrichan S, Phanichphant S. Preparation and Characterization of $BiVO_4$ Powder by the Sol-gel Method. Ferroelectrics. 2013;456:45-54.

[9] Zhang A, Zhang J, Cui N, Tie X, An Y, Li L. Effects of pH on hydrothermal synthesis and characterization of visible-light-driven $BiVO_4$ photocatalyst. J. Mol. Catal. A: Chem. 2009;304:28-32.

[10] Kudo A, Omori K, Kato H. A novel aqueous process for preparation of crystal form controlled and highly crystalline $BiVO_4$ powder from layered vanadates at room temperature and its photocatalytic and photophysical properties. J. Am. Chem. Soc. 1999;121:11459-67.

[11] Hailin T, Huanhuan W, Yanfen F, Ruiping L, Yingping H. Hydrothermal synthesis of m-$BiVO_4$/t-$BiVO_4$ heterostructure for organic pollutants degradation: Insight into the photocatalytic mechanism of exposed facets from crystalline phase controlling. J. Hazard. Mater. 2020;399:123159.

[12] Baral B, Reddy KH, Parida KM. Construction of M-$BiVO_4$/T-$BiVO_4$ isotype heterojunction for enhanced photocatalytic degradation of Norfloxacine and oxygen evolution reaction. J. Colloid Interface Sci. 2019;554:278-95.