Insights from Crystal Size and Band Gap on the Catalytic Activity of Monoclinic BiVO₄

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Abstract—Monoclinic BiVO₄ powders were synthesized from Bi(NO₃)₃.5H₂O and NH₄VO₃ in dilute HNO₃ by homogenous co-precipitation followed by calcination at different temperatures ranging from 350 to 700°C. The effects of increase in the calcination temperatures over the changes in the evaluated physicochemical parameters were bv characterization techniques such as XRD, UV-Vis spectroscopy, Raman analysis and Field Emission Scanning Electron Microscopy (FE-SEM). The parameters responsible for the photochemical water oxidation were studied in detail and it was confirmed from our results that crystalline size and band gap of the BiVO₄ powders are the main responsible for its activity. It is also confirmed from the changes in the intensities and shift in the peak position of Raman analysis, the effect of calcination temperatures over the variations such as lone pair distortions on Bi³⁺ and changes of V-O bond length in the local structure of BiVO₄.

Index Terms—Band gap, crystal size, monoclinic BiVO₄, raman analysis.

I. INTRODUCTION

Development and application of cleaner energy systems play a crucial role towards sustainable development; in particular, increasing CO_2 emissions, environmental impacts and socio-economic issues related with the production, distribution and use of energy sources, call for an urgent improvement of the current available technologies [1]-[3].

Solar energy being the most abundant energy source has been widely exploited for thermal and electrical power generation [1], [4]; however, due to a higher convenience of a means of chemical energy storage, such as H_2 , as compared to electricity, solar fuels have been regarded as one of the most promising technological concepts due to its potential higher efficiency and environmental suitability [5]-[7].

In this context, photocatalytic water splitting into H₂ and O₂ is a topic of increasing interest at present [3], [7]. In order to realize this, the first challenge to be addressed is the accomplishment of the water oxidation half-reaction (2H₂O \rightarrow O₂ + 4H⁺ + 4e⁻), considered as a limiting step since it involves a thermodynamically uphill reaction comprising the simultaneous transference of 4 electrons [2], [8]. Furthermore, development of a catalyst which can utilize whole electromagnetic spectrum is preferred in order to enhance overall water splitting efficiency of photocatalysts [9].

In order to carry out oxidation of water several photocatalysts have been developed and assessed in the last decades [2], [9]-[11] finding out that $BiVO_4$ is one of the most active O_2 evolution photocatalysts in the field of

semiconductor particles and photoanodes [9], [12], due to i) a relatively low band gap of around 2.4 eV for the monoclinic phase [13] enabling the more efficient use of visible light, and ii) an adequate position of the conduction and valance bands as compared to the potential of water oxidation [12]. In addition, $BiVO_4$ is a non-toxic and relatively abundant material [12], [14].

It has been previously reported that among the three occurring phases of BiVO₄, i.e. scheelite-tetragonal (*s*-*t*), zircon-tetragonal (*z*-*t*) and scheelite-monoclinic (*s*-*m*), the latter is the only one that is highly active for O₂ evolution under visible-light irradiation due to its particular crystal and electronic structure [13], [15]. However, currently, there is still an incomplete understanding of the physical properties in BiVO₄ that lead to a high photocatalytic activity, as well as of the formation processes correlated with this phenomena.

Several synthesis methods have been utilized in order to prepare BiVO₄ powders of high quality, predominantly solid-state, aqueous-based and hydrothermal methods [8], [12], [16]-[18]; among them, a simple solution-based preparation method under acidic conditions has been chosen and applied here, involving the calcination of obtained BiVO₄ precipitates at different temperatures. From this, an in-depth analysis of some of the 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 ultimately will lead to the synthesis optimization of more efficient photocatalytic materials.

II. EXPERIMENTAL DETAILS

Samples of BiVO₄ powders were synthesized by dissolving 5 mmol of bismuth nitrate pentahydrate, Bi(NO₃)₃·5H₂O (Sigma Aldrich) in 100 mL of 1M HNO₃ until a clear solution was observed (ca. 30 min.); later 5 mmol of ammonium metavanadate, NH₄VO₃ (Sigma Aldrich) were added to the mixture, which was left for overnight stirring. Precipitate was collected by centrifugation, washed 3 times in distilled water and one time in ethanol, and finally dried at 80 °C overnight. Finally, the samples were calcined in air at different temperatures: 350 °C, 450 °C, 550 °C and 700 °C for 3 hours.

Samples were characterized by X-ray diffraction (XRD) using an X'Pert Phillips diffractometer equipped with Cu K α radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 mA. All the patters were recorded in the range of 5-60^o at a step size of 0.02^o. Crystallite sizes of the samples were estimated by using Scherrer formula [19]:

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

where D is the approximated crystallite size, λ is the wavelength of the X-ray radiation (0.15418 nm); K is the shape factor (0.9); β is the peak width at half-maximum height corrected for instrumental broadening; $2\theta = 30.6^{\circ}$. UV-Vis diffuse reflectance spectra were recorded on a UV-Vis Varian's Cary 5000 spectrophotometer using a quartz cell suitable for powders measurements. The morphology of the samples was investigated by Field emission Scanning Electron Microscopy (FE-SEM) taken with a high-resolution FE-SEM instrument (LEO 1525). Raman spectra were obtained by means of a Renishaw inVia Reflex (Renishaw PLC, United Kingdom) micro-Raman spectrophotometer equipped with a cooled charge-coupled device camera. Samples were excited with an Ar-Kr laser source (648 nm), providing a photon flux lower than 60 W/cm2. The spectral resolution and integration time were 3 cm⁻¹ and 30 s, respectively. All the Raman spectra excited with the same wavelength directly compared in the following sections were recorded at similar conditions.

Photocatalytic O₂ evolution of the samples was carried out from a silver nitrate AgNO₃ (50 mM; 110 mL) solution used as electron acceptor. In a typical test, ca. 100 mg of overnight-outgassed BiVO₄ powders were dispersed in the AgNO₃ solution in a 200cm³ Pyrex reactor cell equipped with an external cooling jacket to maintain a constant temperature. Ar gas was used as a carrier and fluxed in the reactor cell under dark conditions in order to evacuate the air inside, and a constant flow of 12 mL min⁻¹ was kept during the test. The reactor cell was side-illuminated with a simulated solar light by using a plasma lamp (Solaronix model LIFI STA-40), whereas the irradiance of incident light was measured to be 100 mW cm⁻² using a photo-radiometer Delta Ohm model HD2101.1. Illumination was kept during one hour and the amount of evolved O2 was determined in the out-flowing gas using a gas chromatograph (Varian 490-µGC, Molsieve 5A column 10 m, micro-TCD detector) until no traces of O2 were measured, and the cumulative O_2 evolution over 1 h of illumination was estimated by the integration of the GC measurements over time.

III. RESULTS AND DISCUSSION

A. Characterization and Photocatalytic Activity Evaluation

The XRD patterns of BiVO₄ samples calcined at different temperatures are shown in Fig. 1; all these samples exhibit the scheelite-monoclinic (s-m) phase as their diffraction peaks are in good agreement with the standard Joint Committee on Powder Diffraction Standards (JCPDS) card No. 14-0688 (space group: I2/a, a=5.195, b=11.701, c=5.092, β =90.38°). Moreover, all the samples show the characteristic peak splitting diffractions at 2 θ = 18.5, 35 and 46° [20]. Even though monoclinic phase was observed at every calcination temperature, splitting of the these characteristics peaks becomes more pronounced as the calcination temperature increases, which is most likely a sign of the increasing crystallinity degree of the (s-m) phase in BiVO₄ samples [20], [21].



Fig. 1. XRD patterns of the $BiVO_4$ samples synthesized at different calcination temperatures: a) 350 $^{\rm 0}C$; b) 450 $^{\rm 0}C$; c) 550 $^{\rm 0}C$; and d) 700 $^{\rm 0}C$

The FE-SEM images of BiVO₄, powders are given in the Fig. 2. If we have a close look into the pictures significant differences can be observed among the different samples. The samples calcined at 350 and 450° C (a-b) show crystals with well-defined surfaces and a low degree of agglomeration. The powder samples calcined at 550 and 700°C (c-d) showed a clear variation in morphology and degree of agglomeration of particles, probably due to increased sintering at higher calcination temperatures.







Fig. 3. UV-Vis diffuse reflectance spectra of BiVO₄ powders synthesized at different calcination temperatures: a) 350 °C; b) 450 °C; c) 550 °C; and d) 700 °C and inset with Tauc plots showing the effect of calcination temperature on the band gap energy shift.

In order to calculate the electronic states of the semiconductor materials diffuse reflectance spectra (DRS) is used. The DRS of the BiVO₄ samples calcined at different temperatures is shown in Fig. 1. All samples show absorption in the visible region of the electromagnetic spectrum. This gives us information about the monoclinic nature of the BiVO4 samples [13]. The changes in the absorption edges can be observed among the four BIVO4 samples. A red shift was observed among the samples with an increase in the calcination temperature. The band gaps were calculated using Tauc plot and are 2.49, 2.48, 2.41 and 2.39 eV for the samples calcined at 350, 450, 550, 700°C, respectively.

These variations in the samples are in turn responsible for the degree of delocalization of photogenerated electron and hole pairs [18].

Raman spectra of BiVO₄ powders were excited by a red (648 nm) laser and corresponding spectra are shown in Fig. 4. 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 around 210, 324, 366, 640, 710, and 826 cm⁻¹ were observed for all samples. These are the typical vibrational bands of BiVO₄ [18], [20], [22]. The structural information of BiVO₄ is given by the band centered at 210 cm⁻¹. The asymmetric and symmetric formations of VO₄ 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 shift follows a linear trend with the calcination temperature, such as, 825.30, 825.95, 826.62 and 827.59 cm⁻¹ for 350, 450, 550 and 700 °C respectively (Table I). This shift can be correlated to the variations in bond length of the V-O which can be calculated by (2). 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, [23] and [24]:

$$\nu(cm^{-1}) = 21349 \exp(-1.9176 R(A^o))$$
(2)

where v is the stretching Raman frequency for V-O, it can be seen that the bond length varies from 1.6964 to 1.6950A° for 350 to 700 °C samples, respectively.

The synthesized BiVO₄ samples were all investigated to determine their photocatalytic O_2 evolution activity from AgNO₃ solution as sacrificial reagent. The cumulative O_2 evolution of the four samples synthesized at different calcination temperatures is shown in Fig. 5. It is observed that the photocatalytic activity increases with an increase in calcination temperature. The total O_2 evolved after 1 h of illumination under simulated solar irradiation for the samples calcined at 350, 450, 550 and 700^oC was 2.6, 5.6, 17.9 and 57.6 µmol g⁻¹ catalyst, respectively.



Fig. 4. Raman spectra of the BiVO₄ samples synthesized at different calcination temperatures: a) 350 °C; b) 450 °C; c) 550 °C; and d) 700 °C excited by a red-line laser (648 nm)

B. Correlation of O₂ Evolution and Photophysical Parameters of BiVO₄

Herein as per our observations it has been noticed that certain parameters are mainly responsible for water oxidation of $BiVO_4$ powders, such as crystallite sizes that can be acquired from XRD and band gap from UV-Vis spectroscopy. The crystal sizes were calculated according to (1).



Fig. 5. Photocatalytic O₂ evolution from 50 mM AgNO₃ solution (110 mL) under simulated solar irradiation (100 mW cm⁻²) over BiVO₄ powder catalyst (100 mg) calcined at different temperatures

As the calcination temperature increases there is an increase in the crystallite size of the powder samples; moreover there is a good correlation of the increase in the crystalline size and enhancement of O2 evolution, as observed in table I. Even though all samples showed monoclinic phase as per XRD patterns analyzed above, there are differences among the intensities and half-widths of the peaks which describe little variations in the structural parameters of the powder samples. This can be elucidated from the UV-Vis spectra and Raman analysis. The differences in the intensities and peak position of the bands in the Raman spectra clearly demonstrate the variations in the local crystal structure among the powder samples, as the frequencies related to the VO₄ tetrahedron and V-O bonds are directly related to the interactive forces between Bi⁺³ and V⁵⁺ cations. It can be noticed from the relative intensities of the Raman spectra among the powder samples that VO_4^{3-} tetrahedron with different VO_4 space symmetries were formed. It can also be noticed that variations in one of the V-O bond length among the powder samples can be explained on the basis of packing of the structure. The stronger is the packing, shorter is V-O bond length and higher the photocatalytic activity. This can be directly correlated to the lone pair distortion around the bismuth cation as it has a negative effect to the bond length of the V-O. So, there is more distortion of lone pairs in powder samples calcined at 700°C rather than the samples calcined at 350°C. This is an effect that is canceled when we characterize the sample with XRD as it is not sensitive enough to the slight changes in the bond lengths that have an inverse effect.

TABLE I: PHYSICAL PROPERTIES AND O2 EVOLUTION ACTIVITIES OF BIVO4 SAMPLES SYNTHESIZED AT DIFFERENT CALCINATION TEMPERATURES								
Sample	Crystallite Size	Band Gap	Stretching Raman shift	Bond length	Cumulative O ₂ Evolution			

5	ampic	Ci ystainte Size	Danu Gap	V-O ^I	V-O ^I	Cumulative O ₂ Evolution
		[nm]	[eV]	[cm ⁻¹]	[Å]	[µmol h ⁻¹ g ⁻¹ catalyst]
a)	350 ⁰ C	79	2.49	825.30	1.6964	2.6
b)	450 ⁰ C	68	2.48	825.95	1.6960	5.6
c)	550 ⁰ C	80	2.41	826.62	1.6956	17.9
d)	700 ⁰ C	95	2.39	827.59	1.6950	57.6

The band structure in scheelite-monoclinic BiVO₄ is formed by the Bi 6s, O2p and V3d orbitals; among them, valence band is formed by the hybrid of Bi6s and O2p and conduction band by V3d [25]. There is a distinct variation observed in the electronic structure of the samples when the distortion of the VO₄³⁻ tetrahedron occurs. This distortion is due to the lone pair electron of Bi³⁺ in the local structure of the BiVO₄.There is a change in the extent of overlapping of Bi6s and O2p with the distortion of VO_4^{3-} tetrahedron. This overlapping is directly proportional to the degree of distortion which in turn helps in the mobility of photogenerated holes [18]. Thus it can be summarized from XRD, Raman and UV-Vis spectroscopy that increase in crystallinity of powder samples lead to an increase in the delocalization of the electron and hole pairs and a higher overlapping between the Bi6s and O2p orbitals, which finally increases the O₂ evolution of BiVO₄.

IV. CONCLUSION

In our study, it has been confirmed the importance of crystal-size and band gap in correlation with the photochemical water oxidation. The importance of Raman analysis in understanding the variations in a crystal structure is also explained in detail. Thus, keeping in consideration of crystal size to the band gap, one can improve the activity of the BiVO₄ photocatalyst.

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