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# Facile synthesis of nanostructured monoclinic bismuth vanadate by a co-precipitation method: Structural, optical and photocatalytic properties

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ABSTRACT

We report the synthesis of bismuth vanadate ($BiVO_4$) nanostructure by atoxic-free, inexpensive co-precipitation method. The $BiVO_4$ nanostructures were derived from bismuth nitrate and ammonia metavanadate as starting precursors and sodium hydroxide (NaOH) were used as stabilizers for tuning the morphology (nanorod, nanospheriod and nanoparticulate). The influence of post-calcination treatment (450, 550 and 650 °C) on structural, optical and photocatalytic properties of $BiVO_4$ was studied. The post-calcination treatment strongly induces the crystallization process and produce monoclinic $BiVO_4$ structure with predominant (112) crystallite phases. The absorbance of $BiVO_4$ shows broad coverage of visible light wavelength region up to 550 nm, which is appreciable for solar light driven photocatalysis. Among the different calcinated samples, anisotropy rod-shape $BiVO_4$ (calcinated at 450 °C) shows high optical absorbance than other treated (550 and 650 °C) samples. The monotonic shift in characteristic Raman vibration mode at 824 $cm^{-1}$ with increasing calcination temperature indicates that the V–O bond length is affected by $Bi^{3+}$ diffusivity. The PL spectra of these samples explore the intrinsic defects present in BiVO4, and found to be high in high temperature calcinated samples. The photocatalytic property of resultant $BiVO_4$ samples was evaluated in oxygen generation with $Ag^+$ donors. As a result of reduced defects and high optical absorbance, the $BiVO_4$ calcinated at 450 °C showed high photocatalytic oxygen yield (1.02 mmol) compared with high temperature calcinated samples (0.48 mmol).The appreciable quantity of solar fuel $O_2$ generation from the low-cost co-precipitation method can be widely implemented in other visible light metal oxide nanostructures.

## 1. Introduction

Developing the photocatalytic semiconductor materials find great deal of attention in recent years owing to their pronounced progress in many applications including fuel

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generation [1], water purification [2–4], anti-microbial activity [5,6], self-cleaning coating [7,8], environmental remediation (NOx removal) [9,10] and biosensors [11,12]. In particular, decomposition of water into hydrogen and oxygen by utilizing photocatalytic materials at unassisted bias condition has triggered huge body of scientific research towards solar to fuel generation around the globe [1]. Recently, suspended photocatalysis with visible light semiconductor driven by solar light afford substantial yield of $H_2$ and $O_2$ without any adverse effect ($CO_2$ emission) to the environment, endorsing an appropriate system for green fuel generation [13,14]. In the available literature, titanium dioxide ($TiO_2$) showed an impressive yield in solar fuel generation of 6.6 l/m$^2$ per day with reliable stability [15]. However, large intrinsic band gap of 3.2 eV result high photoactivity only under UV wavelength region. Therefore, improving the visible light activity of $TiO_2$ has become one of the major tasks in solar fuel generation using $TiO_2$. Conversely, developing new photocatalytic systems capable of accessing the visible light is gaining momentum in materials science aspect. In this context, bismuth vanadate ($BiVO_4$) is considered as an important semiconductor in solar fuel generation, owing to their prevailing absorbance band edge position in visible wavelength region (2.4 eV) [16,17]. More importantly, the biocompatibility of $BiVO_4$ is an appreciable choice in toxic-free indoor photocatalytic coatings. The more positive valence band (VB) edge position of $BiVO_4$ compared to water oxidation potential 1.23 V RHE could drive highly active visible-light-driven photocatalyst for $O_2$ evolution with the quantum yield of 9% at 450 nm [16,18]. The photoexcited electrons from conduction band of $BiVO_4$ are injected to collector terminal with aid of external applied bias, whereas the photoholes will be involved in a water oxidation process. However, conduction band energy of $BiVO_4$ lies below the water reduction potential (0 V vs RHE), which could limit the overall hydrogen generation. Therefore, the $BiVO_4$ exhibits effective photoelectrocatalytic $H_2$ generation in combination with suitable catalyst (Pt, Ru) [19–21] and co-catalyst (Co–Pi, FeOOH) [22–24] materials. In addition, doping carries (Mo and W) also could promote the photocatalytic water oxidation process through facilitating the charge separation ($e^-/h^+$) at $BiVO_4$ under light irradiation, and thus overwhelm the recombination process. Recently, Abdi et al. demonstrated a competitive solar to hydrogen efficiency (STH) of 4.9 % in $BiVO_4$ system compare to p–n type tandem photocatalyst through achieving the formation of distributed $n^+$–n homojunction by W doping [25].

The $BiVO_4$ exists in three types of polymorphs including Scheelite structure with monoclinic (s–m), tetragonal (s–t) phases, and zircon structure with tetragonal (z–t) phase. Among the three phases, monoclinic structure shows feasible photocatalytic activity than other structures due to its relatively narrow band gap of 2.4 eV compared to tetragonal structure (3.1 eV) [26]. Monoclinic-$BiVO_4$ has been synthesized via different methods like homogeneous precipitation [27], co-precipitation [28], surfactant-assisted [29], sonochemical method [30], sol–gel process [31], reverse-micro emulsion technique [32], and hydrothermal treatment [33–36]. Based on the earlier reports the photocatalytic performance of $BiVO_4$ mostly depends with crystallite phase governs with (a) visible light property, (b) electronic structure and (c) photocarrier transport properties. Therefore to design the efficient $BiVO_4$ photocatalyst the choice of experimental technique plays a vital role in the aforementioned properties. In view of large scale production, the co-precipitation method is an appropriate method in producing large quantity of target material at low-cost. Despite the low processing temperature environment and less expensiveness of the co-precipitation method than other experimental methods, ammonia is widely used as stabilizing agent, which is hazardous to health and thus limits the large scale synthesis. Therefore, developing monoclinic-phase $BiVO_4$ at low cost without using toxic reagents is highly demanded in view of producing green photocatalytic materials. In this report, we report the facial synthesis of M-$BiVO_4$ through the toxic-free, co-precipitation method using NaOH as stabilizing agent to tailor the wide range of morphology. Also, we investigate the temperature-dependent structural and optical properties, and analyzed their influence on the photocatalytic property of M-$BiVO_4$ in aqueous solution.

## 2. Materials and methods

### 2.1. Chemicals

The following chemicals were used as received without further purification. Bismuth nitrate pentahydrate (Loba Chemie, India), Ammonium metavanadate (SD Fine, India), nitric acid (Merck), and sodium hydroxide (Merck) were used. The deionized ultra-pure distilled water was used in all synthesis processes.

### 2.2. Facile synthesis of $BiVO_4$ nanostructured powder

The $BiVO_4$ powder was prepared as follows: first, 0.1 M of $(BiNO_3)_3$ $5H_2O$ and 0.2 M of $NH_4VO_3$ were added with 40 ml of diluted $HNO_3$. The mixed solution was continuously stirred by applying minimum temperature of 50 °C until the solids were completely dissolved. A transparent yellow homogeneous solution was obtained. Now the pH value was adjusted to basic condition (pH = 10) with the addition of NaOH solution. A yellow precipitate was formed. The resultant yellow precipitate was separated by filtration and washed with distilled water several times to remove the impurities and residual materials. Then, the resultant precipitate was heated in the open hot plate to ensure the evaporation of all water contents. Finally, the mixture was cooled to room temperature and the powders were calcinated at 450 °C, 550 °C and 650 °C for 3 h.

### 2.3. Characterization

The crystallite phases of $BiVO_4$ powders were studied by X-ray diffraction (X'PERT PRO PANanalytical) using the Cu Kα wavelength of 1.54060 Å in a $2\theta$ range of 10–80° with a step size of 0.0500 (degree/s). The X ray tube is operated at 30 mA and 40 kV.To study the surface morphology of the powders the scanning electron microscopy (SEM) (VEGA3 TESCAN) with energy dispersive analysis (EDS) (Bruker) was used. The optical absorbance and reflectance of the $BiVO_4$ powders