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**HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF BISMUTH
VANADATE PHOTOCATALYST**

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Abstract

Particulate photocatalyst for hydrogen production by water splitting and water purification has received a great attention because of their low cost and applicability in mass scale. Bismuth vanadate (BiVO_4) has recently emerged as one of the most promising photocatalysts for hydrogen production via water splitting and degradation of pollutants. Based on previous studies, it's well established that pure monoclinic (m)- BiVO_4 has showed the best photocatalytic performance so far. In this investigation, pure m- BiVO_4 nanoparticles have been synthesized in a hydrothermal synthesis process: $(\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/\text{V}_2\text{O}_5/\text{K}_2\text{SO}_4, 200^\circ\text{C})$. It is demonstrated that formation of pure m- BiVO_4 with less impure phases is enhanced by addition of an inorganic morphology controlling agent (K_2SO_4) in system has been demonstrated. $\text{Bi}_{(1-x)}\text{Nd}_x\text{VO}_4$ and $\text{BiMn}_x\text{V}_{(1-x)}\text{O}_4$ (where $x = 0.10$) nanoparticles have been synthesized to investigate the effects of doping on the structural formation, optical bandgap, particle size and morphology of particulate BiVO_4 . In $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/\text{V}_2\text{O}_5/\text{K}_2\text{SO}_4, 200^\circ\text{C}$ system, $\text{BiMn}_x\text{V}_{(1-x)}\text{O}_4$ and $\text{Bi}_{(1-x)}\text{Nd}_x\text{VO}_4$ were formed as pure m- BiVO_4 and a small presence of zircon type BiVO_4 was found in $\text{Bi}_{(1-x)}\text{Nd}_x\text{VO}_4$ (where $x = 0.10$). The reason of a slight increase in bandgap energy of $\text{Bi}_{(1-x)}\text{Nd}_x\text{VO}_4$ (where $x = 0.10$) has also been explained. In future, the synthesized bismuth vanadate nanoparticles will be used for photocatalytic degradation of dyes.

Keywords: Bismuth vanadate, Hydrothermal synthesis, Artificial photosynthesis, X-Ray diffraction, Optical bandgap

1. INTRODUCTION

With the rapid increase in population, the demand of energy is increasing day by day. Major portion of this demand is supplied by fossil fuels which has led to destruction of global environment in many ways. Water pollution has become one of the most alarming concerns among them. Research on water splitting and degradation of organic pollutants may be the green alternative technologies to solve this challenge where photosynthesis – the capture, conversion and storage of solar energy in chemical bonds plays as the design key. But we can utilize small percentage of solar energy which is very much insufficient for natural photosynthesis. For this reason, an innovation of a photocatalyst with practical application has become a crying need to the researchers all over the world.

Since the discovery of water splitting phenomenon by Fujishima and Honda [1], the quest for developing such photocatalyst has remained still unsatisfied to the researchers. Several binary and ternary oxides have been developed such as TiO_2 , Ag_3VO_4 , InNbO_4 , InVO_4 , and BiVO_4 . Among these oxides, BiVO_4 has attracted as most promising and suitable choice for its non-toxic nature and formation in various synthesis routes including conventional solid state reaction, sol-gel, coprecipitation, hydrothermal process, chemical bath deposition and hybrid organic-inorganic routes [2-6]. Bismuth vanadate has mainly three crystalline phases: monoclinic scheelite, tetragonal scheelite and tetragonal zircon structures. Park et al reported monoclinic scheelite phase bismuth vanadate (m- BiVO_4) as the most promising visible light absorbing photocatalyst [7]. But in most synthetic process, the synthesized nanoparticles have large crystal sizes and low surface areas [8-9]. Therefore, a search for developing m- BiVO_4 with large surface area and high photocatalytic activity is still going on. Y. Zhou *et al* stated that in their hydrothermal process (in $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/\text{V}_2\text{O}_5, 200^\circ\text{C}$ system), formation of m-

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BiVO_4 with less impure phases is enhanced by addition with an inorganic morphology controlling agent (K_2SO_4) [10].

In our present work, pure m- BiVO_4 has been synthesized in a straightforward hydrothermal process, the difference of the addition of K_2SO_4 is again investigated and later in $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/\text{V}_2\text{O}_5/\text{K}_2\text{SO}_4$, 200 °C system, $\text{BiMn}_x\text{V}_{(1-x)}\text{O}_4$ and $\text{Bi}_{(1-x)}\text{Nd}_x\text{VO}_4$ (where $x = 0.10$) have been synthesized to study the effect of doping on structural formation, optical bandgap and particle morphology. These findings may be used for further studies on photocatalytic activities of bismuth vanadate.

2. EXPERIMENTAL

2.1 SYNTHESIS

In the typical procedure of synthesis, 97 mg $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.2 mmol) and 36.38 mg V_2O_5 (0.2 mmol) were taken as 1:1 molar ratio in a beaker with 10 mL water and 1 gm K_2SO_4 (5.7 mmol) were added at room temperature. After 5 minutes of magnetic stirring, the resulting precursor suspension was then transferred into a Teflon lined stainless steel autoclave with a capacity of 25 mL, maintained at 200 °C for 24 h and cooled at room temperature naturally. The precipitate was then collected after centrifugation at 4000 rpm for 5 minutes and dried in air. This sample is referred as sample S2 in the text. In order to investigate the effect of K_2SO_4 addition on formation of m- BiVO_4 and effect of doping on m- BiVO_4 , three more samples are synthesized, where Bi is substituted by 10% Nd in S3 and V is substituted by 10% Mn in S4. Parameter details are shown in table 1.

Table 1: Preparative parameters of synthesized samples of BiVO_4

Sample No	Sample	Precursor	Molar Amount	Weight	Temperature
S1	BiVO_4	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ V_2O_5 H_2O	0.2 mmol 0.2 mmol	97 mg 36.38 mg 10 mL	200 °C
S2	BiVO_4	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ V_2O_5 K_2SO_4 H_2O	0.2 mmol 0.2 mmol 5.7 mmol	97 mg 36.38 mg 1 gm 10 mL	200 °C
S3	$\text{Bi}_{0.9}\text{Nd}_{0.1}\text{VO}_4$	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ Nd_2O_5 V_2O_5 K_2SO_4 H_2O	0.18 mmol 0.01 mmol 0.2 mmol 5.7 mmol	87.3 mg 3.68 mg 36.38 mg 1 gm 10 mL	200 °C
S4	$\text{BiV}_{0.9}\text{Mn}_{0.1}\text{O}_4$	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ V_2O_5 $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ K_2SO_4 H_2O	0.2 mmol 0.18 mmol 0.01 mmol 5.7 mmol	97 mg 32.742 mg 25.101 mg 1 gm 10 mL	200 °C

2.2 ANALYTICAL CHARACTERIZATION

Powder X-ray diffraction (XRD – Empyrean, PANalytical, Netherlands) of the synthesized nanoparticles was carried out within a 2θ range of 10° to 70° for the crystal structure analysis and phase identification. Particle size and morphology was observed adopting field emission scanning electron microscope (FESEM – JSM 7600, JEOL, Japan). The optical bandgap energies of the synthesized samples were measured from diffused reflectance spectra using a UV-Vis spectrometer (UV/Vis/NIR – Lambda 1050, PerkinElmer, USA).

3. RESULTS AND DISCUSSIONS

The formation of monoclinic (m)- BiVO_4 in hydrothermal synthesis technique completely depends on synthesis parameters. Therefore, fine tuning of m- BiVO_4 formation during synthesis is quite difficult due to its quick response on any reaction conditions. Y. Zhou *et al* reported that $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and V_2O_5 are the appropriate bismuth and vanadium precursors and addition of K_2SO_4 as an inorganic morphology controlling agent significantly influences the particle morphology [10]. It is also reported that m- BiVO_4 with less impure phases are formed in the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/\text{V}_2\text{O}_5/\text{K}_2\text{SO}_4$ system [10]. The use of BiCl_3 can form VCl_2 as side product and NaBiO_3 generates products with an irregular morphology. We have observed the related effect, the PXRD patterns of BiVO_4 samples which are prepared by hydrothermal synthesis process are shown in fig 1.

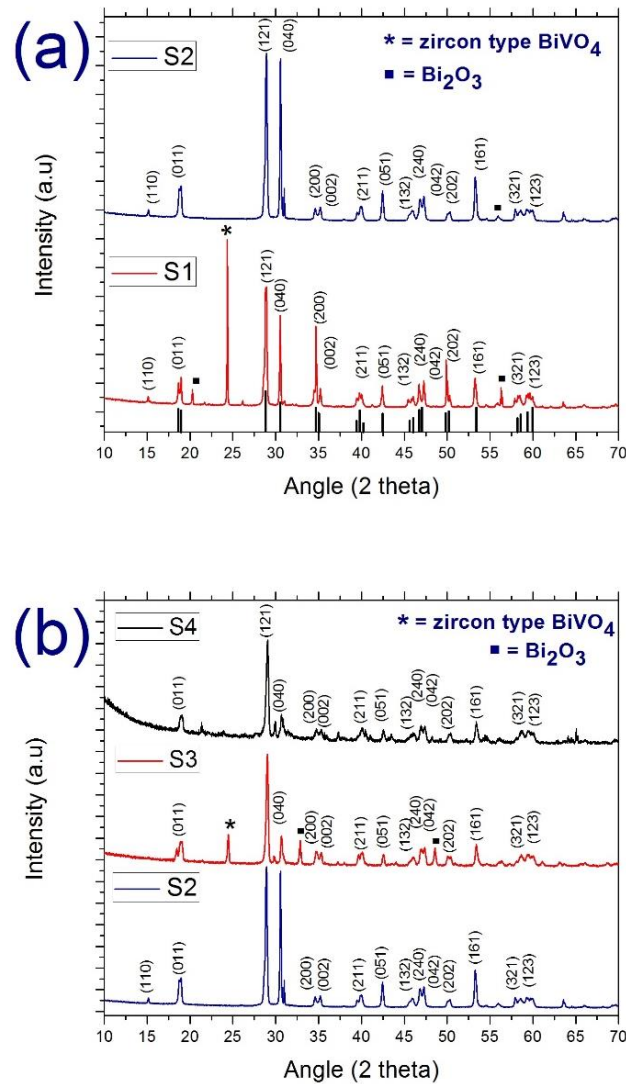


Fig.1: PXRD pattern of synthesized BiVO_4 obtained from different parameter variations (table 1). (a) PXRD pattern of S1 and S2. The reference pattern of monoclinic BiVO_4 (JCPDS No. 75-2480) is shown at the bottom. (b) PXRD pattern of S2, S3 and S4.

The BiVO_4 samples which are prepared in absence of K_2SO_4 and in presence of K_2SO_4 are denoted as sample S1 and S2 respectively. In fig 1 (a), it's clearly observed that in absence of K_2SO_4 , impure phases are appeared in S1. The strong peak at $2\theta = 24^\circ$ confirms the presence of tetragonal zircon phase in S1 sample [11]. All the peaks for BiVO_4 (1) are in good agreement with pure monoclinic scheelite BiVO_4 (JCPDS No. 75-2480).

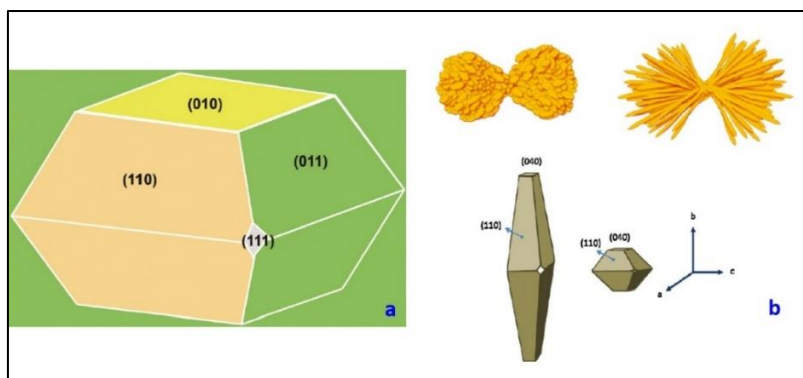


Fig 2: (a) Typical crystal of BiVO₄ exposed with the {010}, {110}, {011} and {111} facets (reproduced from ref 12, copyright The Royal Society of Chemistry, 2014). (b) Schematic illustration of different morphologies of BiVO₄ (reproduced from ref 13, copyright Elsevier B.V. 2011)

This is further confirmed by the splitting of the peaks at $2\theta = 18.5^\circ$, 35° and 46° which are the characteristic peaks of m- BiVO₄. Interesting results have been noticed in fig 1 (b), where PXRD patterns for sample Bi_{0.9}Nd_{0.1}VO₄ and BiMn_{0.1}V_{0.9}O₄ are shown and compared with sample BiVO₄ (2). In Nd doped BiVO₄, the small presence of tetragonal zircon BiVO₄ is noticed. Except this, all the peaks for two doped samples can be indexed to m- BiVO₄ which confirms the successful formation of Nd and Mn doped m- BiVO₄. From fig 1 (b), it is evident that the peak at $2\theta = 31.5^\circ$ has suppressed after doping at bismuth site (Nd doped BiVO₄) and at vanadium site (Mn doped BiVO₄). This peak is responsible for (040) crystal plane. So, in doped sample, the particle will be either equal edge pallet shaped or needle shaped. This assumption totally matched with the images obtained from FESEM.

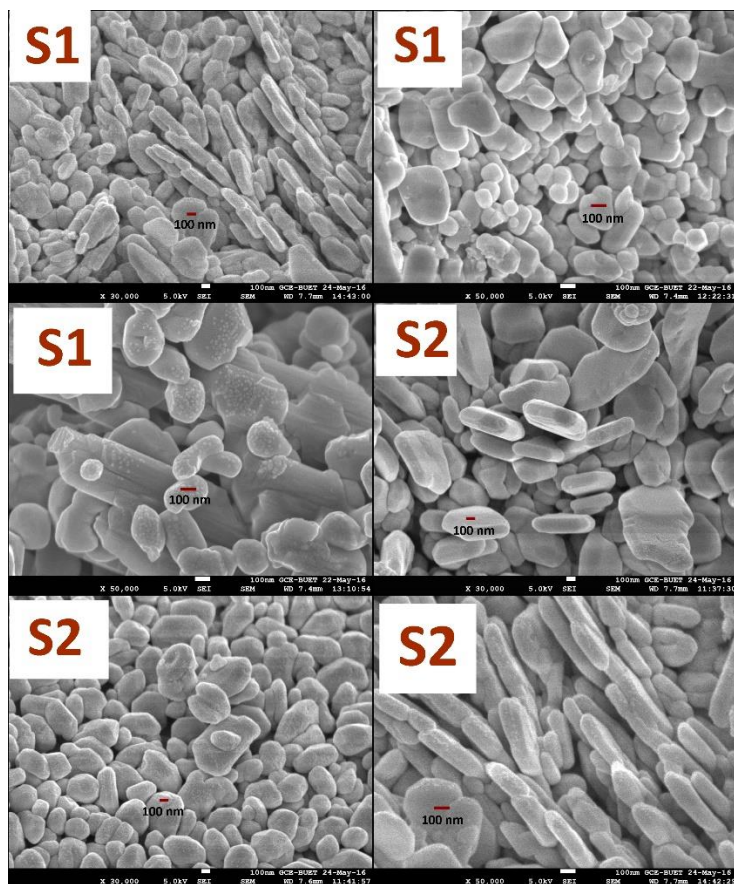


Fig 3 (a): FESEM micrographs of sample S1 and S2.

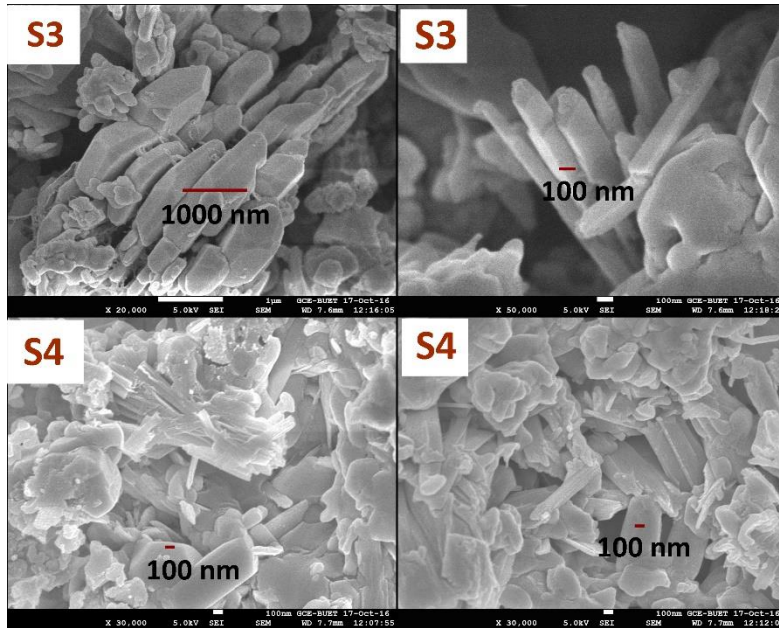


Fig 3 (b): FESEM micrographs of sample S3 and S4.

Fig 4 shows the absorption vs wavelength plot of doped and undoped samples. This diffused reflectance data was converted to Kubelka-Munk function [14] given by

$$F(R) = \frac{(1-R)^2}{2R} \quad (1)$$

(where R is the diffused reflectance value) to construct $[hvF(R)]^2$ vs photon energy (hv) plots of BiVO_4 samples (fig 5).

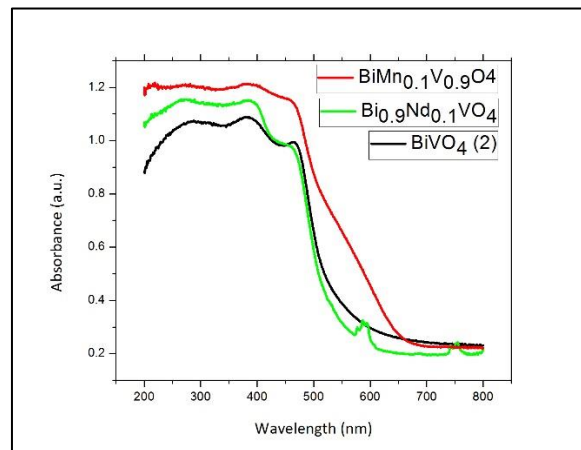


Fig 4: UV-Vis absorption spectra of sample S2, S3 and S4.

The intersection of the tangent line with $[hvF(R)]^2 = 0$ represents the optical band gap energy. Fig 5 shows that the band gap of sample S2, S3 and S4 are 2.47 eV, 2.5 eV and 2.44 eV respectively.

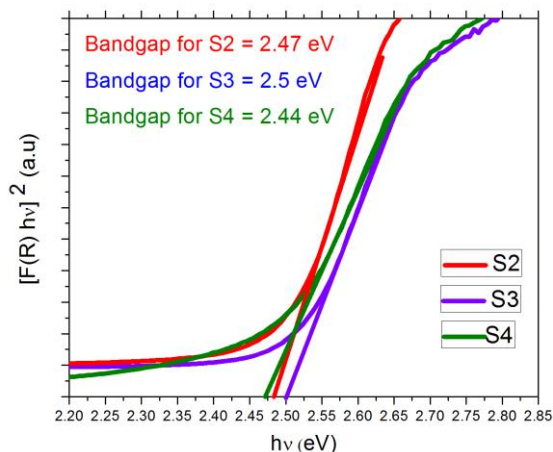


Fig 5: $[hvF(R)]^2$ vs photon energy ($h\nu$) plots to calculate band gap energy of the samples (a) S3 (b) S2 (c) S3.

In scheelite structures, each V ion is coordinated by four O atoms in a tetrahedral site and each Bi ion is coordinated by eight O atoms from eight different VO_4 tetrahedral units [16]. Each O atom in this structure is coordinated to two Bi centers and one V center, holding the Bi and V centers together forming a three dimensional structure. The only difference between the tetragonal and monoclinic scheelite structure is that the local environments of V and Bi ions are more significantly distorted in monoclinic scheelite structure, which removes the four fold symmetry necessary for a tetragonal system.

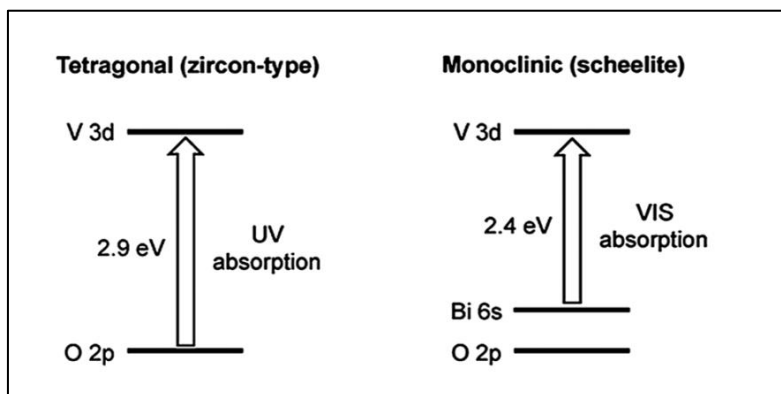


Fig 6: Schematic band structures of the tetragonal zircon type $BiVO_4$ and monoclinic scheelite $BiVO_4$ proposed by Kudo et al. (Reproduced from ref 15. Copyright 1999, American Chemistry Society)

In the zircon type $BiVO_4$, the bandgap transition takes place due to the charge transfer transition from O 2p orbitals to empty V 3d. In scheelite structure, bandgap is reduced because 6s state of Bi^{3+} remains above O 2p orbital and transition from Bi 6s² to V 3d becomes possible. Density Functional Theory (DFT) calculations by Walsh *et al.* showed that hybridization between the Bi 6s state and the O 2p state at the top of the VB is indeed responsible for the relatively smaller bandgap of $BiVO_4$ with a monoclinic scheelite structure [17]. They explained that $BiVO_4$ has a direct bandgap and its VB is composed of O 2p with Bi 6s contributing to the top region of VB. This interaction of O 2p and Bi 6s at the top region of VB has antibonding nature.

In our experiment, fig 1 (b) clearly indicates that there is no zircon type $BiVO_4$ present in sample S2 and S4. All peaks are in perfect match with pure m- $BiVO_4$. But in S3, a small presence of zircon type $BiVO_4$ was found and except this, rest peaks indicate the formation of m- $BiVO_4$. Very small amount of impure phases are found in synthesized samples as it's mentioned earlier that formation of pure m- $BiVO_4$ is quite difficult due to its quick response to the reaction conditions.

Kudo *et al.* reported that the bandgap energies for scheelite and zircon type BiVO_4 is 2.4 eV and 2.9 eV respectively [6]. For S2 and S4, the bandgap energies are almost close to the theoretical value. But for sample S3, the bandgap is slightly increased (2.5 eV) due to presence of some zircon type BiVO_4 along with major amount of m- BiVO_4 .

5. CONCLUSIONS

In this report, it's investigated that in the presence of inorganic morphology controlling agent (K_2SO_4), pure m- BiVO_4 can be synthesized with less impure phases in a straightforward hydrothermal process. It's clearly shown that no significant alteration in optical bandgap or structural formation takes place in $\text{BiMn}_x\text{V}_{(1-x)}\text{O}_4$ and $\text{Bi}_{(1-x)}\text{Nd}_x\text{VO}_4$ (where $x = 0.10$). A slight increase in S3 has been noticed due to formation of small amount of zircon type BiVO_4 . The photocatalytic experiment needs to be carried out to investigate photocatalytic performance of these synthesized (both doped and undoped) nanoparticles.

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