Structural and Optical properties of Molybdenum doped Bismuth vanadate powders

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Abstract—**Molybdenum doped $BiVO_4$ powders were prepared by Sol-gel method. Monoclinic scheelite phase was confirmed from X-ray diffraction (XRD) patterns and micro-Raman vibrational bands. Substitution of molybdenum in crystal sites of $BiVO_4$ was evidenced from XRD by higher angle 2θ shift of the characteristic peak (-121) and from Raman showing lower frequency shift of dominant peak from 831 to 822 cm^{-1} which corresponds to V-O symmetric stretching mode. The morphological properties were analyzed by FE-SEM which confirmed the formation of homogeneous spherical shaped particles with size around 200-300nm. Optical properties were analyzed by Diffuse Reflectance Spectra which show higher absorption in the range of 550-850nm. Optical band gap energies were calculated by using Kubelka- Munk formula, *i.e*, 2.46 eV for 2 wt% Mo- $BiVO_4$ and 2.47eV for undoped $BiVO_4$. This confirms that, $Mo-BiVO_4$ particles have the same band gap but induce higher absorption in visible light region compared to $BiVO_4$.**

Keywords: Sol-gel, $BiVO_4$, Molybdenum doping, Raman, Diffuse reflectance spectra.

I. INTRODUCTION

The search for efficient visible light driven photocatalyst for water splitting or decomposition of organic contaminations has led to an upsurge in the field of photocatalysis. In last two decades, TiO_2 (titanium di-oxide) is widely used photocatalyst because of its efficiency and stability in aqueous media [1], However, it is active only under UV radiation and absorbs only 4-6% of sunlight [2]. Recently, $BiVO_4$ as a visible light driven photocatalyst has received significant attention as prospect for water splitting and water detoxification applications [3-5]. The main factors required for an efficient semiconductor photocatalyst are the band gap (Eg), the rate of electron-hole generation and the lifetime of excitons. However, there are many other factors which can affect the performance and upsurge efficiency of the photocatalyst, such as depth of penetration of incident light, carrier mobility, effective charge transfer, life span of photo-generated charge carriers (holes and electrons) and their transportation rate from surface of catalyst to solution species [6]. Thus, it is obvious that crystallographic structure and composition of photocatalyst plays a major role in photo catalysis. According to previous reports, $BiVO_4$ appears in three main crystalline phases: monoclinic scheelite, tetragonal scheelite and tetragonal zircon [7, 8]. However, monoclinic $BiVO_4$ is expected to be more efficient due to a narrow band gap (ca. 2.4 eV) monitored by the energy transition from a valence band being composed by hybridized orbitals of Bi 6s and O 2p to a conduction band (CB) populated from V 3d orbital [9]. However, the photocatalytic behavior of pure $BiVO_4$ is still low due to poor quantum yield and moderate diffusion length of photo- excited carriers [10]. To circumvent this problem, doping is an efficient method to enhance photocatalytic performance as suggested by first principle DFT calculations [20]. $BiVO_4$ was modified by doping with non-metals [23], transition metals [11-13], rare earth metal [14, 15] and noble metals [16-19]. Metal doping contributes significantly to the formation of impurity energy levels inside the band gap. This enhances the promotion of electrons in CB and then the efficiency of photocatalysis. Molybdenum (Mo) atom has one excess valence electron as compared to Vanadium (V) atom. So, doping of Mo contributes to shallow impurity energy levels which require low energy for electron injection in CB [20] leading to an increase in the electrical conductivity of $BiVO_4$. Substitutional doping $Mo-BiVO_4$ has shown remarkable enhancement in water oxidation and degradation organic pollutants reported by Yao et al [28].

From experimental side, Mo doped $BiVO_4$ are synthesized by several chemical routes, such as Sol-gel [22, 26], hydrothermal [23], Co-precipitation [21] and impregnation method [24, 25]. However, sol–gel process is one of the most widely used methods because the easy synthesis, low processing temperature, good control on composition and better homogeneity of the final solids. In this report, visible light driven photocatalyst as $Mo-BiVO_4$ powders were synthesized by using sol-gel technique in the aim of applications for degradation of organic pollutants in aqueous media.

II. EXPERIMENTAL PROCEDURE

Sol-gel synthesis of $Mo-BiVO_4$ powders was performed by using 0.485g (0.01mol) of $Bi_2(Ni_3)_3 \cdot 5H_2O$ dissolved in 100 mL of 10% (w/w) nitric acid. Then, 0.384g (0.02 mol) of citric acid as a chelating agent was added to form a solution A. Similarly, 0.181g (0.01 mol) of NH_3VO_4 was dissolved in 50ml distilled water at 80 °C and 0.02 mol of citric acid was added to form a solution B. Solution A was added drop-wise into solution B

under vigorous stirring to make a C. 2 wt% of Molybdenum microparticles as dopant were added to solution C. Under vigorous stirring, the pH of mixture was adjusted to approximately 6.5. The mixture was stirred at 80 °C until the dark blue sol-gel was obtained, and then the sol-gel was dried at 80°C. The final product was obtained from dried powder by calcination at three different temperatures at 100, 300 and 500^oC during 2 hours.

III. CHARACTERIZATION TECHNIQUES

X-ray diffraction (XRD) patterns of Mo-BiVO4 samples were recorded on an X-ray powder diffractometer (PANanalytical system) which was operated at 40 kV and 35 mA using Cu $K\alpha$ radiation (λ=1.5418Å). The morphologies of the samples were observed using a scanning electron microscope (JEOL, JSM 6510) operating at 20 kV. Micro-Raman measurements were performed using a LabRAM Jobin Yvon spectrometer with a 632.8 nm He-Ne laser source. The UV-visible diffuse reflectance spectra were recorded at room temperature with a UV-Visible spectrometer (UV-2500, Shimadzu) and converted to an absorbance spectrum by the Kubelka–Munk method.

IV. RESULTS AND DISCUSSION

A. X-ray powder diffraction analysis:

The unit cell of monoclinic phase of $BiVO_4$ (space group: C2/b, space group number 15) contains four bismuth (Bi) and four vanadium(V) atoms coordinated with 16 oxygen(O) atoms. The coordination consists in dodecahedron as BiO_8 and tetrahedron as VO_4. Diffraction patterns of Mo-$BiVO_4$ powders exhibited pure monoclinic Scheelite phase structure (JCPDS No.14-0688) which was correlated with $BiVO_4$ shown in **Fig.1**   The insert shows that the superimposition of characteristic peaks at 2θ = 28.5851, 28.8211, 28.945 corresponding to (hkl) planes as (-130), (-121) and (121) were slightly shifted (ca.0.1°) in comparison with un-doped $BiVO_4$. This shift indicates the occurrence of compression strain induced in clinobisvanite system with variation in the lattice dimensions [27] (further justified by Raman analysis) by the incorporation of Molybdenum in monoclinic structure of $BiVO_4$. This is caused by the ionic radii of V^{5+} (0.050 nm) (in tetrahedral coordination) being close to the substitutional Mo^{6+} (0.055 nm) in the same tetrahedral arrangement [29]. It is well known the lattice exhibits distortions with doping elements into the crystal host sites. Lattice dimensions and atomic position were calculated for Mo-$BiVO_4$ and $BiVO_4$ by Reitveld method using MAUD software. Refined parameters were shown in table 1 and table 2 respectively. The compressed unit cell of Mo-$BiVO_4$ is due to the substitution of Mo in few sites of V as reflected through the positional change of V, O1 and O2, while Bi didn't show any structural effect. These data confirms the substitution of tetrahedral coordinated V by Mo ions in the crystal lattice. The Mean size of crystalline domains of Mo-$BiVO_4$ and un-

doped $BiVO_4$ were calculated from Scherrer's formula (Eqn-1) as shown in Table3 along with optical energy band gap measurement values. Scherrer's formula has follows

$$\tau = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

Where, $'\tau'$ is the mean size of the ordered domains (crystallite size); $'K'$ is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.891, but varies with the actual shape of the crystallite; λ is the X-ray wavelength Cu Kα=0.154 nm; β is FWHM of peak at particular plane in radians. $'\theta'$ is the Bragg's angle.

The line broadening was measured by using a standard diffraction pattern of LaB_6 (Lanthanum Hexaboride powder). Instrumental broadening measured as 0.046 degrees in 2θ was subtracted from the FWHM observed diffracted patterns by using equation (2).

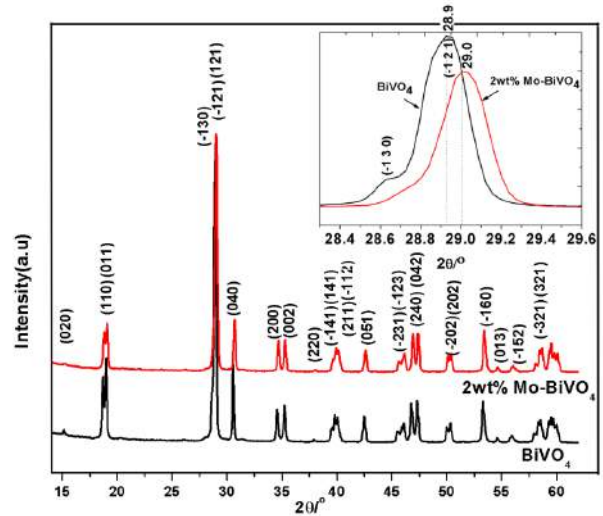$$FWHM_{2\theta} = \sqrt{(FWHM)^2_{observed} - (FWHM)^2_{LaB_6}} \qquad (2)$$

Figure 1: XRD pattern of Mo- $BiVO_4$ by sol gel method in comparison with undoped $BiVO_4$. Insert shows characteristic peak shift to higher angle 2θ position.

Table 1: Refined lattice dimensions of 2wt% Mo-$BiVO_4$ and $BiVO_4$ respectively.

Sample	a(Å)	b(Å)	c(Å)	γ(º)	Volume of cell (10^6 pm^3)
BiVO4	5.195	5.093	11.704	90.38	309.74
2wt%Mo-BiVO4	5.173	5.087	11.661	90.32	307.58

Table 2: Atomic positions of 2wt% Mo-$BiVO_4$ and $BiVO_4$ samples from rietveld refinement.

Sample	Bi	V	O_1	O_2
BiVO4	0, 0.25, 0.6337	0 0.25 0.1352	0.149, 0.506, 0.210	0.258 0.379 0.451
2wt%Mo-BiVO4	0, 0.25, 0.6275	0.05, 0.255, 0.104	0.121, 0.483, 0.184	0.249, 0.414, 0.450

Table 3: Crystallite size and energy band gaps of Mo-BiVO$_4$ and undoped BiVO$_4$ samples respectively.

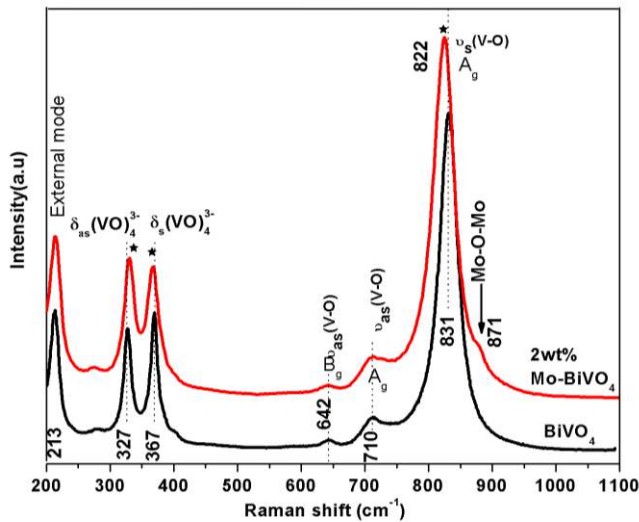| Samples	FWHM$_{2\theta}$	2θ position (-121)	Crystallite size(nm)	Band gap E_g(eV)
BiVO$_4$	0.240	28.92	34.5	2.47
2wt%Mo-BiVO$_4$	0.242	29.01	33.8	2.46

Figure 2: Raman spectra of 2wt% Mo-BiVO$_4$ compared to undoped BiVO$_4$

B.Raman analysis:

Raman spectroscopy is a non-destructive spectroscopic technique to study vibrational, rotational, and other low-frequency modes of both organic and inorganic samples. Raman spectra of clinobisvanite have five noticeable distinctive vibrational modes around 213, 327, 367, 710 and 831cm^{-1} which reflects VO$_4$ tetrahedon in monoclinic BiVO$_4$ system. Major Raman modes A$_g$ at 831 and 710 cm^{-1} can be assigned to the symmetric and asymmetric stretching modes of V–O bonds in VO$_4$ tetrahedron respectively [28]. The symmetric and anti-symmetric bending modes are observed at 367 and 327cm^{-1} respectively, and external modes occur at 213cm^{-1}. For Mo-BiVO$_4$ the V-O stretching mode has shifted to a lower frequency (822 cm^{-1}) as compared to 831 cm^{-1} for BiVO$_4$. This is understood by substitution of V by Mo in VO$_4$ tetrahedron, with clear increment of V-O bond length [28]. This is also confirmed by the presence of Mo-O-Mo stretching mode at ca.871cm-1.

C. Morphology studies:

The surface morphology and particle size were observed by Field Emission-Scanning electron microscopy(FE-SEM) for 2wt%Mo-BiVO$_4$ and BiVO$_4$ samples, shown in Fig.3. Spherical shaped agglomerated particle with size around 300 nm for BiVO$_4$, while smaller, but more homogeneous, spherical shape particles of around 200- 300 nm are observed for Mo-BiVO$_4$. The smaller size of the Mo-BiVO$_4$ particles confirms that doping inhibits the particle growth. Furthermore, the chemical composition of Mo-BiVO$_4$ and BiVO$_4$ sample were displayed in table.2, which confirms the presence of Mo along with Bi, V, O elements in BiVO$_4$ system.
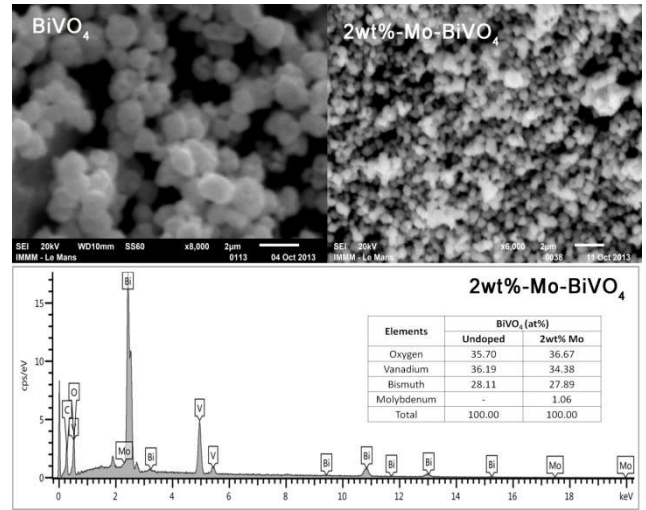

Figure 3: SEM images of Mo doped BiVO$_4$ and undoped BiVO$_4$ with EDAX composition in inset

D. DRS analysis:

UV-visible diffuse reflectance spectra of Mo-BiVO$_4$ and BiVO$_4$ are shown in Fig.4. Mo-BiVO$_4$ induces more absorption in the range of 500-850 nm as compared to BiVO$_4$. The substituted Mo doped BiVO$_4$ forms impurity energy levels by hybridization of 4d obitals of Mo and the 2p orbital of oxygen between the VB and CB. These regions are attributed due to bonding and antibonding features of Mo-O bonds [30]. Therefore, the band edge positions VBM and CBM will change without modifying the bandgap and optical absorption wavelength threshold [20]. This band edge position changes will lead to lower effective mass of carriers, implying higher mobility of photoinduced carriers. Subsequently, an enhancement is expected in the photocatalytic performance under visible light irradiation. These results have been corroborated from experimental calculations [29]. The optical band gap measurements were determined by using an approximate form of Kubelka-Munk model from equation (3).

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s} = \frac{Ac}{s} \qquad (3)$$

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Where R is absolute reflectance of the sample, k the molar absorption coefficient, s the scattering coefficient, c is the concentration of the absorbing species and A the absorbance.

The calculated energy band gaps of $BiVO_4$ and Mo doped $BiVO_4$ are 2.47eV and 2.46 eV respectively. The formation of impurity energy levels by introducing doping atoms as Mo into $BiVO_4$ host lattice will facilitate consecutive electron-hole generation which occurs within the visible region, improving then the exploitation of large spectral range of solar emission.
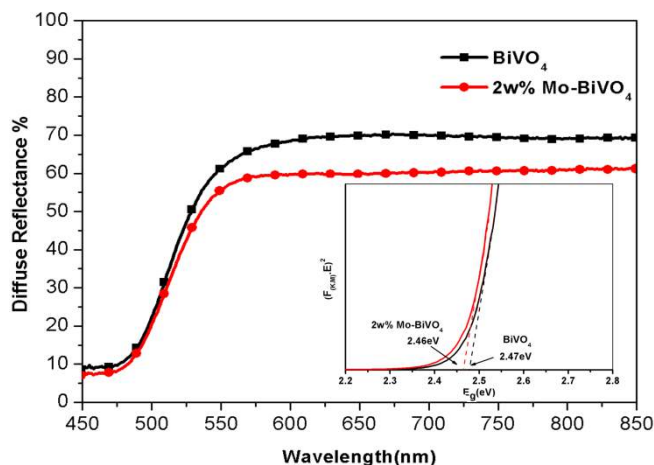

Figure 4: DRS spectra of 2wt% Mo-$BiVO_4$ along with $BiVO_4$. In insert, the calculated energy band gaps from Kubelka-Munk model.

V. CONCLUSIONS

Mo doped $BiVO_4$ nanoparticles were synthesized by Sol-Gel route. Mo substitutional doping has been confirmed by XRD and micro-Raman analysis. An additional support is traduced from the higher absorption in the range of 550 -850 nm while the band gap remains unchanged. Mo-$BiVO_4$ has shown smaller size particles compared to $BiVO_4$ particles which leads higher surface area able to enhance the photocatalytic performance under visible-light irradiation. This improvement is based on an increase of charge carriers and higher mobility of photo induced carriers by change in band edge positions of $BiVO_4$ through the hybridized 4d orbitals of Mo and the orbitals 2p of oxygen. The investigation of photocatalytic activity of Mo doped $BiVO_4$ are underway.

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