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Enhancement of photocatalytic activity of $BiVO_4$ by barium doping

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$BiVO_4$ has been successfully synthesized by solid state method and doped by barium in the sites of bismuth in 3%, 6%, 9% and 15% to form $Bi_{1-x}Ba_xVO_4$ (x = 0.03, 0.06, 0.09 & 0.15). The products have been characterized using powder X-ray diffraction, diffuse reflectance spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy and photoluminescence spectroscopy. The band gap of undoped $BiVO_4$ is calculated to be 2.19 eV and the barium doped $BiVO_4$ compounds exhibit band gaps which are closer to the band gap of undoped compound. The photocatalytic activities of undoped and doped catalysts for the degradation of methylene blue have been studied using UV-visible spectroscopy and found to be depended largely on the barium content and the particle size of the compounds.

Keywords: $BiVO_4$, Photocatalysis, Degradation of pollutants; Barium doping

Metal oxides exhibit interesting properties which are preferable for various applications such as catalysis, magnetism, sensors and so on[1]. Metal oxides such as $BiVO_4$, Bi_2WO_6, Bi_2MoO_6 are well known for their potential catalytic activity especially in the decomposition of various pollutants in the water bodies. These materials can be used for the treatment of pollutants in waste water or industrial effluents to replace the commercially used TiO_2[2-6]. Apart from these, carbon based materials, phosphates and framework materials are also investigated for their potential activity[7-11]. These catalytic materials can be utilized for the treatment of pollutants in waste water if they are effectively modified[12-14]. This approach can give a solution to the severe water pollution caused by the industrial effluents especially the textile dyes, as the release of colored compounds in water bodies turned to be a threat for the environment. It affects the water quality and living organisms because of the carcinogenic nature of these compounds. Such problems demand a proper treatment of the polluted water using suitable catalysts. Among many available catalysts $BiVO_4$ shows interesting properties to be considered as the effective photocatalyst for the waste water treatment[15-18]. This material can be synthesized using variety of methods such as solid state reactions, hydrothermal, sol-gel method and so on[19-21]. Different methods can yield different types of properties to the material.

Among these the solid state reactions are preferable due to the involvement of less emission of harmful by-products and also there are no solvents or toxic chemicals used. But the solid state synthesis also has certain limitations such as high reaction temperature, producing larger particles and low catalytic activity[22-24]. If the catalysts can be prepared using the environmentally friendly solid state method and their activity can be enhanced that would provide a more realistic route to degrade pollutants like textile dyes for their application in waste water treatment. This work focuses on solid state preparation of $BiVO_4$ and attempts were made to enhance the catalytic activity by doping and modifying reaction conditions. Doped $BiVO_4$ compounds were investigated as photocatalysts in the presence of visible light/sun light for the degradation of methylene blue which was taken as a model system.

Materials and Methods

Synthesis

Starting materials for the preparation of catalyst Bi_2O_3, V_2O_5 & $BaCO_3$ were purchased from Sigma-Aldrich. Hydrogen peroxide and methylene blue were purchased from S. D. Fine Chem-Limited. All the chemicals were procured as analytical grade reagents and used without any further purification. Stoichiometric amounts of Bi_2O_3 and V_2O_5 powders were taken in an agate mortar and grinded for 45 min to mix the starting materials and to make the mixture as homogeneous as possible. Then, this mixture was heated at 700 ^{o}C for 8 h continuously. The heating and cooling rates were 5 ^{o}C/min and

2 °C/min, respectively. Barium doped samples were prepared, by using $BaCO_3$ along with other starting materials in the required quantity and following similar conditions.

Characterization

Powder X-ray diffraction patterns were collected at room temperature using PANalytical X-ray diffractometer which is equipped with Cu-Kα radiation (λ = 0.1542 nm) at a voltage of 40 kV and a current of 30 mA. Raman spectra of all the samples were recorded on a Horiba, LabRAMHR(UV) instrument. Diffuse reflectance spectra and absorption spectra were recorded using Shimadzu UV-260 spectrophotometer. Scanning electron microscopy and energy-dispersive spectroscopy studies were done with the help of TESCAN-VEGA3 LMU SEM under accelerated electron beam with 30 kV energy. For EDS measurements, random spots from the sample were chosen for the analysis and the average atomic percentage of each element was calculated. Photoluminescence studies were carried out using Hitachi F-7200 fluorescence spectrophotometer ranging from 200 to 600 nm.

Photocatalysis

Photocatalytic experiments under visible light for the degradation of methylene blue dye solutions were carried out with 0.5 g of the respective catalysts. Concentration of the dye solution was 15 ppm and 250 ml of the dye was taken for each experiment. A specially designed reactor with 250 W high pressure mercury lamp (OSRAM MBF-U E-40) with magnetic stirrer was used for the photodegradation studies. The samples were placed at a distance of 20 cm from the light source. At the given time intervals 10 ml of the sample was taken and centrifuged to get a clear supernatant liquid which was further analyzed by UV-visible spectroscopy. Similarly, photocatalytic experiments were also performed in the presence of sunlight with the same amount of dye solution and catalyst.

Results and Discussion

Structural analysis

The powder X-ray diffraction of undoped and doped $BiVO_4$ samples were recorded from 10 to 60° using as prepared samples, which is shown in Fig. 1a. Powder X-ray diffraction pattern shows the formation of monoclinic phase of $BiVO_4$ as it is matching well with the JCPDS file no. 14-688 with space group: I2/a. Peaks of tetragonal $BiVO_4$ were not observed in the diffraction pattern which supports the formation of only the monoclinic phase. Formation of monoclinic phase is significant as the tetragonal phase exhibits poor catalytic activity. Presence of any fraction of tetragonal phase can reduce the overall catalytic efficiency. Doped $BiVO_4$ samples were successfully synthesized using the solid state reactions where the conditions to prepare were same as that of parent compound. But, some of the doped samples show the presence of small amount of impurity. 3% and 6% doped $BiVO_4$ compounds are free from the impurities but 9% and 15% doped samples show the presence of Bi_2O_3 as an impurity phase which comes from the unreacted starting material. The peaks at 28.2°, 31.8° and 32.3° are the peaks from the Bi_2O_3 impurity whereas the other peaks belong to the monoclinic

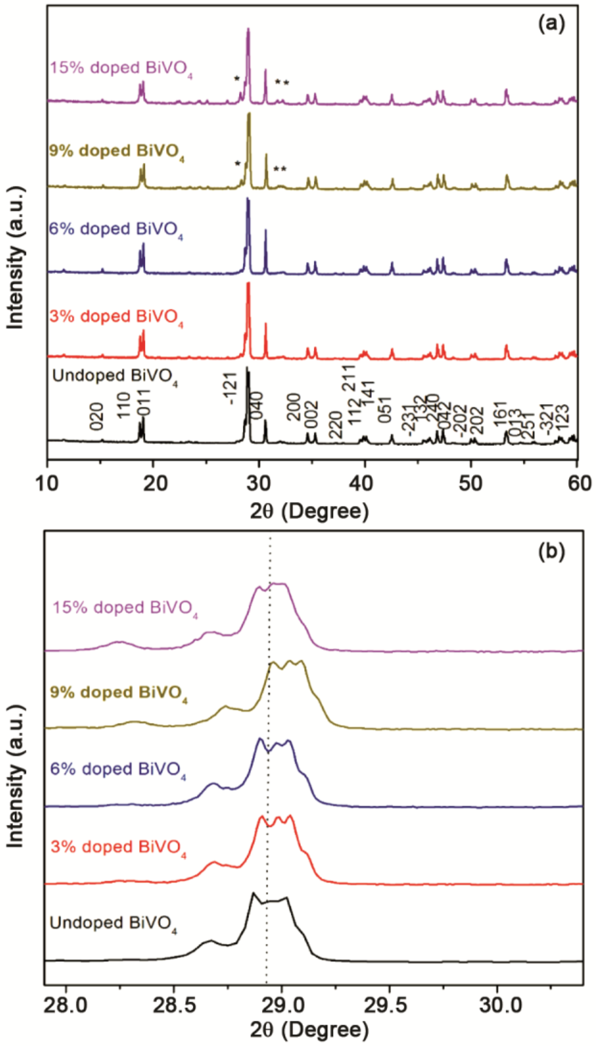

Fig. 1 — (a) Powder X-ray diffraction pattern of undoped and barium doped $BiVO_4$ (* indicates the Bi_2O_3 impurity) and (b) Enlarged view of the most intense peak around 28.9°.

BiVO$_4$. The calculated lattice parameters using XRD patterns and the comparison of the as synthesized catalyst along with the used catalyst are shown in the Supplementary Data (Table S1 and Fig. S1). The doped samples are not showing appreciable shifts in powder XRD which is shown in Fig. 1b, where the most intense peak of monoclinic BiVO$_4$ around 28.9°, is not showing any such shifts. In this study, powder XRD is not sensitive to analyze small changes due to doping. To analyze this further, the more sensitive Raman spectra was recorded.

Raman studies

Raman spectra of undoped and barium doped compounds, exhibited the characteristic peaks as reported in the literature[25-26] which is shown in Fig. 2a. Band corresponding to the symmetric V-O stretching mode at 827.7 cm^{-1} and the asymmetric V–O stretching mode at 713.1 cm^{-1} are observed for the monoclinic BiVO$_4$. Bands corresponding to the external modes at 125.3 and 211.9 cm^{-1} are observed along with the symmetric and asymmetric bending modes of vanadate units (VO_4^{3-}) around 329.3 and 368.6 cm^{-1}, respectively. The intensity of the band for symmetric V-O stretching mode at 827.7 cm^{-1} decreases as the amount of dopant increases. This trend is due to the substitution of Bi^{3+} ions by the Ba^{2+} ion which leads to the deformation of VO$_4$ tetrahedron. Similar effects are reported when the Bi^{3+} sites are doped by Co^{2+} and Fe^{3+} ions in monoclinic BiVO$_4$[27-28]. A small shift towards lower frequencies is also observed for higher concentration of barium (9 and 15%) in the symmetric stretching mode which is shown in Fig. 2b. This effect is observed because the larger Ba^{2+} ions (1.35 Å) are replacing smaller Bi^{3+}ions (1.03 Å) which can cause deformation and surface defects. Similar trend is reported when Bi^{3+} sites are doped by Ni^{2+} ions[29]. Hence, it is evident from Raman studies that the bismuth sites are partially replaced by barium ions.When Ba^{2+} ions replace the sites of Bi^{3+} that can lead to an imbalance in the overall charge which can be balanced by oxygen vacancies or formation of V^{4+}. These possibilities are proven in the literature by XPS analysis, when metal ions (M^{2+}) with similar charge such as Co^{2+} or Ni^{2+}replaces the Bi^{3+} sites of BiVO$_4$[27 & 29].

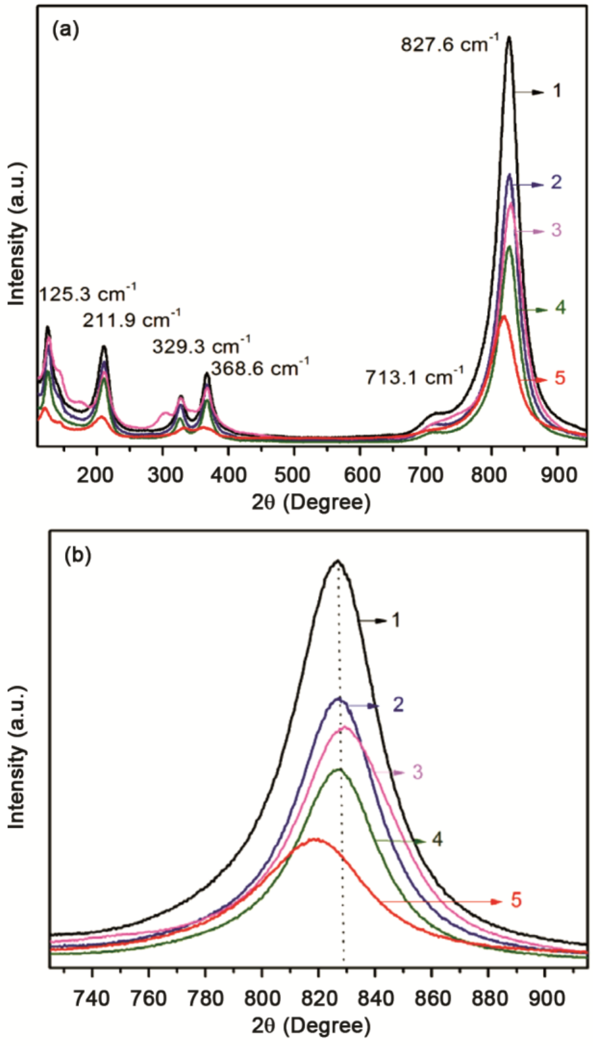

Fig. 2 — (a) Raman spectra of doped and undoped compounds, (1) undoped BiVO$_4$, (2) 3% doped BiVO$_4$, (3) 6% doped BiVO$_4$, (4) 9% doped BiVO$_4$ and (5) 15% doped BiVO$_4$ and (b) Symmetric V-O stretching mode of vanadate unit, showing the shift for compositions containing higher barium content.

Morphological studies

Scanning electron microscopic images of all the as prepared samples are shown in Fig. 3. BiVO$_4$ particles show irregular sphere like and plate like morphologies. The doped samples show irregular morphologies. The particles of undoped and doped BiVO$_4$ are in the order of few micrometers (1 – 5 μm) except the 15% doped sample which has particles in few hundred nanometer scale. Particle size can be directly related to the catalytic activity and so the 15% barium doped sample is expected to show the highest catalytic activity among all due to the availability of more surface area. Energy dispersive X-ray spectroscopy (Fig. S7 and Table S3, Supplementary Data) is also performed for all the prepared samples. All the elements were identified including the barium atoms which were used for the doping that suggests the presence of dopant in all the doped samples. No contamination from container (alumina) was observed.

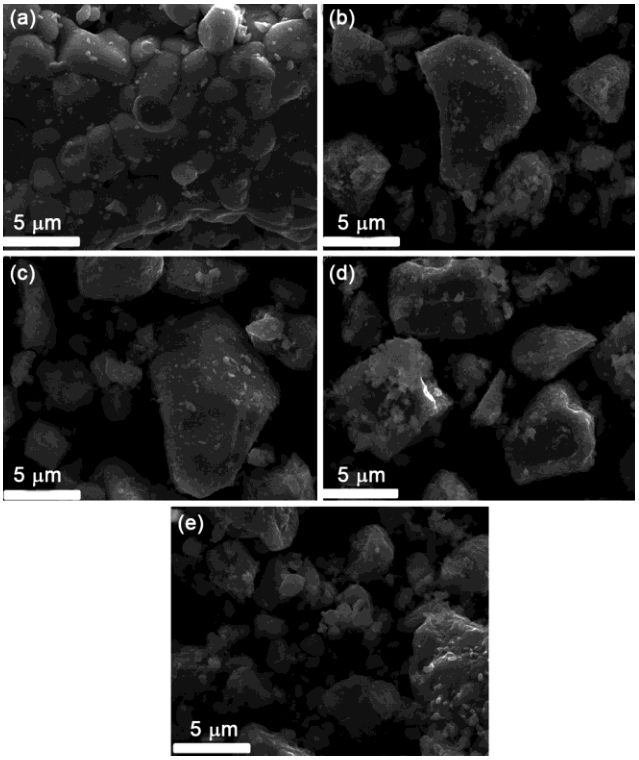

Fig. 3 — Scanning electron microscopy images of (a) undoped $BiVO_4$, (b) 3% doped $BiVO_4$, (c) 6% doped $BiVO_4$, (d) 9% doped $BiVO_4$ and (e) 15% doped $BiVO_4$.

Optical studies

Band gap of all the prepared compounds were determined using diffuse reflectance spectroscopy. Tauc plots were drawn which were further extrapolated to calculate the direct band gaps of the catalysts that are shown in Fig. 4. Undoped $BiVO_4$ shows a band gap of 2.19 eV which is closer to the reported value[30-32] and the band gaps of other doped catalyst are not showing much deviation from this. Though, usually doping changes the band gaps by modifying the band structure, in few cases the effect of dopant becomes insignificant as the changes are trivial. In copper and nickel doped $BiVO_4$, the change in band gap is too small that can be correlated to the observation in barium doped compounds[26,29]. This indicates doping is not significantly affecting the band structure or band gap when Ba^{2+} ions replace some of the Bi^{3+} sites. All these compounds can act as visible light catalysts. Table 1 shows the band gaps of each of the prepared compounds. Photoluminescence spectra of all the samples were recorded in the range of 380– 650 nm. It was observed that $BiVO_4$ shows strong emissions which are centered at 500, 549 and 608 nm. The behavior of $BiVO_4$ is similar to the already reported studies[33]. Effective separation of electrons and hole is the key factor to achieve high photocatalytic activity and this is observed by the drastic fall in the emission intensities of doped samples of $BiVO_4$ that indicates the possibility of possessing potential photocatalytic activity[34]. Fig. 5 shows the photoluminescence spectra of all the prepared catalysts.

Photocatalytic studies

Photocatalytic activities of $BiVO_4$ and barium doped $BiVO_4$ were investigated for the photocatalytic degradation of methylene blue in aqueous solution where the concentration of the dye solution was 15 ppm for all the experiments. Prior to the photocatalytic experiments, adsorption effect was studied by stirring the dye solution with catalyst for 12 h in dark which is not showing any significant reduction in the concentration of the dye solution (Supplementary Data, Fig S2). Apart from that, before starting every experiment, the catalyst was stirred along with the dye solution for atleast 30 min in the dark, to obtain adsorption-desorption equilibrium and the concentration of the dye solution was observed to be same afterwards. This observation ensures that the adsorption of dye on the surface of catalyst is insignificant in terms changing concentration. The photocatalytic degradation of methylene blue by $BiVO_4$ and barium doped $BiVO_4$ were carried out in the reactor (using 250 W, high pressure mercury lamp) and sunlight which are shown in Fig. 6 and 7, respectively. Catalyst loading was also varied to find the optimum weight of catalyst to be used. When the weight was more than 0.5 g, no appreciable increase in photocatalytic efficiency was observed and when the weight was less than 0.5 g there was reduction in efficiency. Thus, usage of 0.5 g of catalyst was fixed for all the experiments. Photocatalytic degradation of methylene blue by as prepared $BiVO_4$ was 8 % in 120 min and in case of doped samples, 15% doped $BiVO_4$ exhibit the highest degradation efficiency of 15% in 120 min. 3%, 6% and 9% doped compounds exhibit 11%, 10% and 13%, respectively efficiency to degrade the 15 ppm dye solution in 120 min. Photocatalytic activity of $BiVO_4$ and barium doped $BiVO_4$ were comparatively lower in the reactor. The effect of temperature was also studied from 40 to 70 °C and it was observed that the increase in temperature has no significant effect on catalysis. Similarly, the effect of pH was also studied where the acidic and alkaline pH levels (from 4 to 8) were maintained and the catalytic efficiency could not be

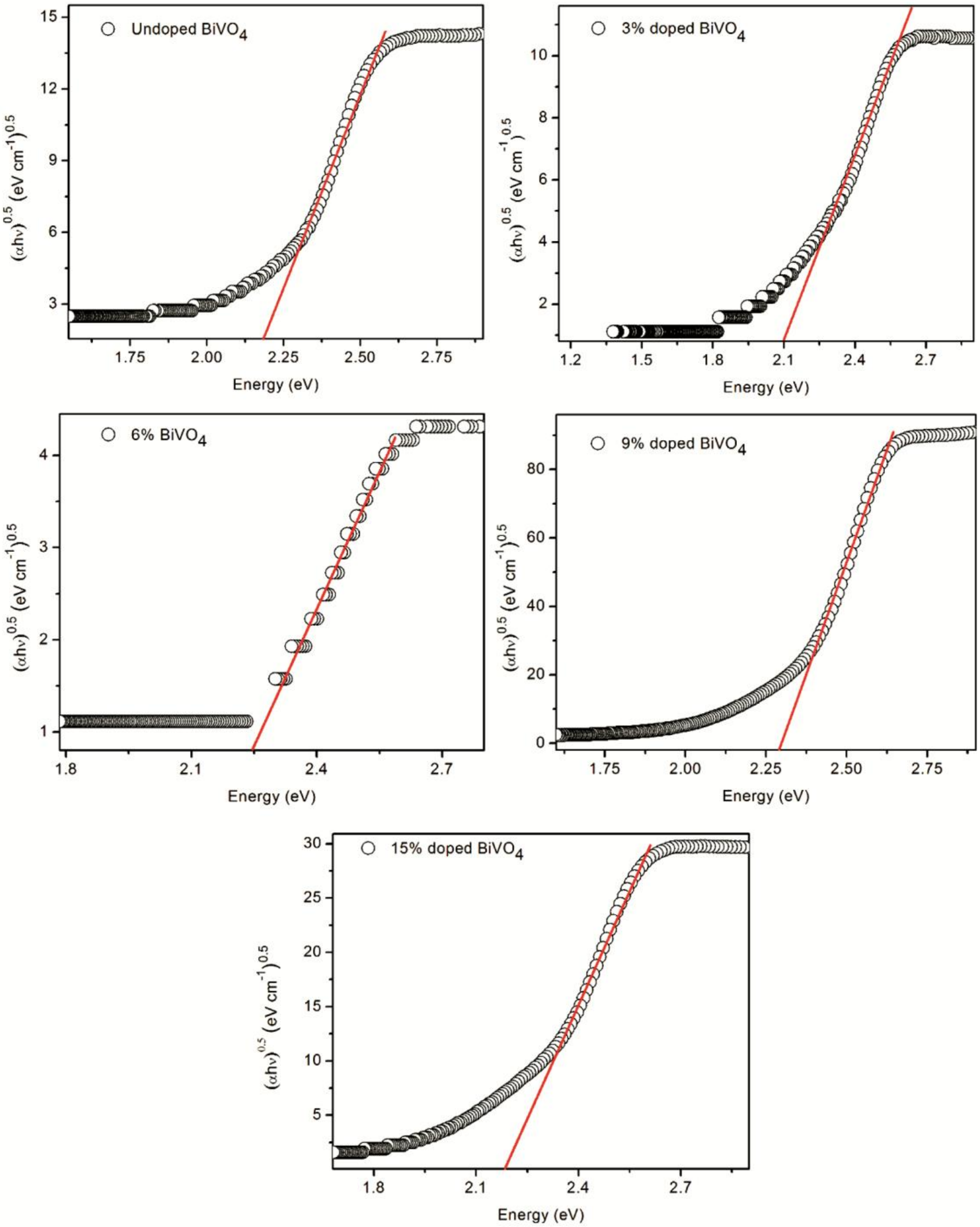

Fig. 4 — Band gap of undoped and doped BiVO$_4$ compounds calculated using diffuse reflectance spectroscopy and extrapolation method.

Table 1 — Band gap of undoped and doped BiVO$_4$ samples calculated using diffuse reflectance spectra

Compounds	Band gap (eV)
Undoped BiVO$_4$	2.19
3% doped BiVO$_4$	2.10
6% doped BiVO$_4$	2.24
9% doped BiVO$_4$	2.29
15% dopedBiVO$_4$	2.19

improved. Then similar experiments were conducted (without changing the pH) in the presence of sunlight and found to show better activity. Efficiency of undoped BiVO$_4$, 3%, 6%, 9% and 15% doped BiVO$_4$ were increased up to 43%, 46%, 48 %, 57 % and 62 %, respectively in 300 min. In sunlight, all the catalysts were showing higher activity towards the degradation of the dye.

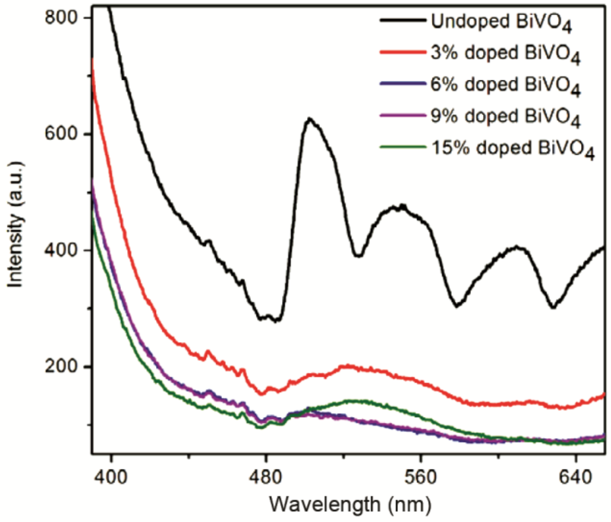

Fig. 5 — Photoluminescence spectra of doped and undoped $BiVO_4$.

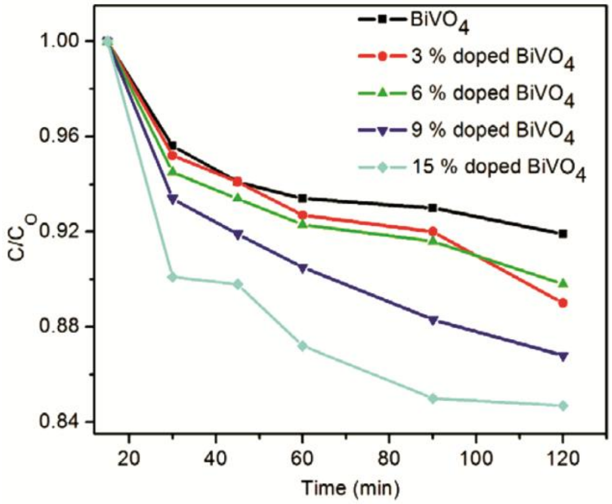

Fig. 6 — Photocatalytic degradation of methylene blue by undoped and doped $BiVO_4$ (3%, 6%, 9% and 15% Ba doped $BiVO_4$) in the reactor.

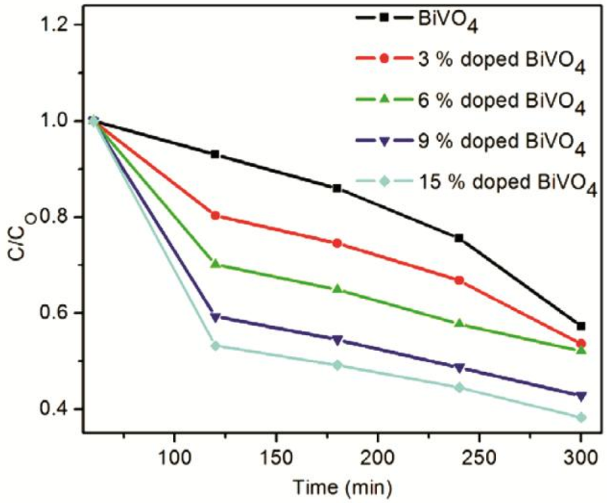

Fig. 7 — Photocatalytic degradation of methylene blue by undoped and doped $BiVO_4$ (3%, 6%, 9% and 15% Ba doped $BiVO_4$) in the presence of sunlight.

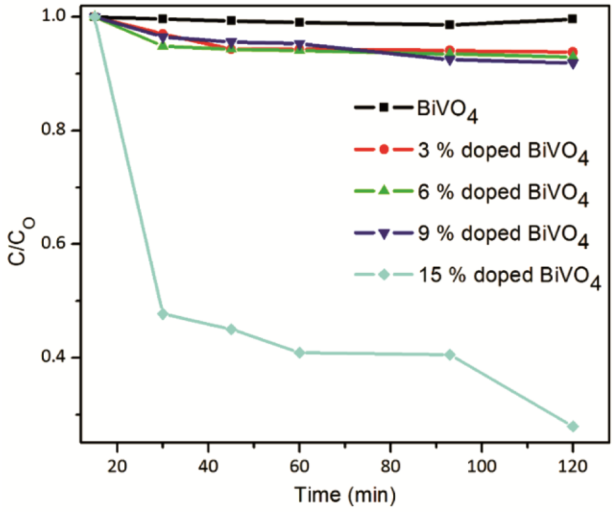

Fig. 8 — Photocatalytic degradation of methylene blue by undoped and doped $BiVO_4$ (3%, 6%, 9% and 15% Ba doped $BiVO_4$) in the reactor along with H_2O_2.

The mechanism of photodecomposition of dye is reported in previous literature[35-37] where the formation of hydroxyl radicals plays a key role in the degradation of dyes. Addition of hydroxyl radical generators or electron acceptors like hydrogen peroxide was studied in few reports,[38-40] and it is observed that this can enhance the catalytic efficiency. The enhancement of photodegradation rate by the addition of hydrogen peroxide is attributed to two factors, (i) hydrogen peroxide acts as an electron acceptor to reduce the recombination rate of the photogenerated electron hole pairs (ii) enhancement of rate of hydroxyl radical generation. Hence, in this study, the effect of addition of H_2O_2 to the reaction mixture was investigated. 2 ml of H_2O_2 was added to the 15 ppm of methylene blue aqueous solution and the catalyst load was 0.5 g. Fig. 8 and 9 show the photocatalytic degradation of methylene blue by $BiVO_4$ and doped $BiVO_4$ along with 2 ml of H_2O_2, in the reactor and in the presence of sunlight, respectively. In the presence of H_2O_2 photocatalytic efficiency of methylene blue by $BiVO_4$ in reactor is comparatively lower than in sunlight. The efficiency of $BiVO_4$ is 43% when the same experiment is conducted in sunlight. Almost complete decolorisation of methylene blue occurs in 300 min, when 15% barium doped $BiVO_4$ was used as a catalyst.

Table 2 — Photocatalytic efficiencies of all the prepared samples at different conditions

Compounds	In reactor (120 min)	In reactor+ H_2O_2 (120 min)	In sunlight (300 min)	In sunlight H_2O_2 (300 min)
$BiVO_4$	08 %	02 %	43%	43%
3% doped $BiVO_4$	11 %	06%	46%	46%
6% doped $BiVO_4$	10 %	07 %	48 %	48 %
9% doped $BiVO_4$	13%	08 %	57 %	66%
15% doped $BiVO_4$	15%	72 %	62 %	100 %

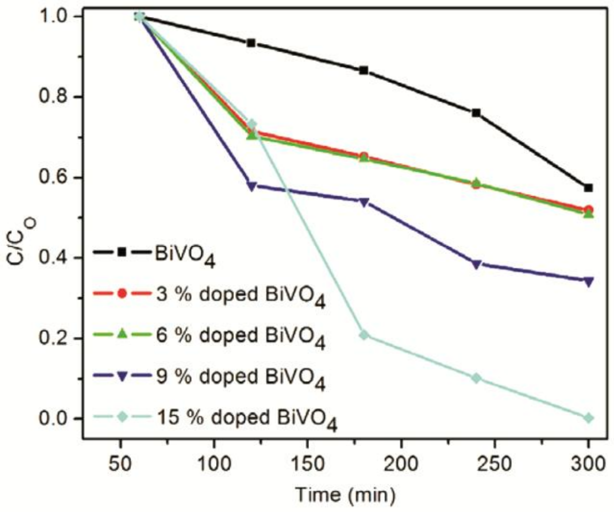

Fig. 9 — Photocatalytic degradation of methylene blue by undoped and doped $BiVO_4$ (3%, 6%, 9% and 15% Ba doped $BiVO_4$) in the presence of sunlight along with H_2O_2.

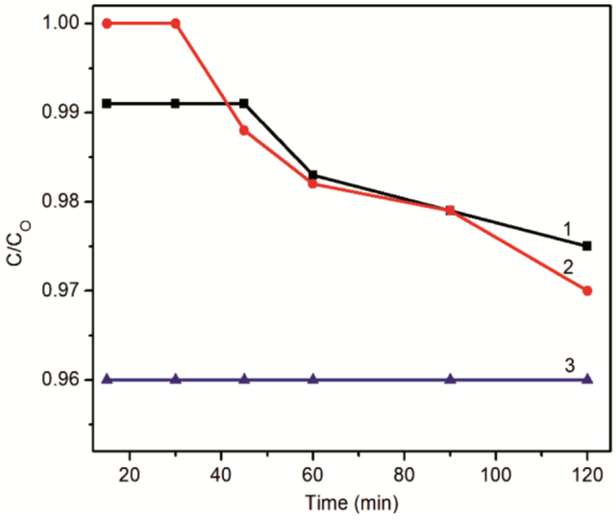

Fig. 10 — Degradation of methylene blue in other conditions,(1) photolysis of MB without using the catalyst or H_2O_2 (2) photodegradation of MB by H_2O_2without using the catalyst and (3) Degradation of MB by the catalyst in the absence of light.

Table 2 shows the photocatalytic efficiencies of all the prepared compounds towards the degradation of methylene blue in different conditions. Fig. 10 explains that H_2O_2 alone cannot show any photocatalytic activity towards the degradation of methylene blue. Only when H_2O_2 is combined along with the catalyst shows better photocatalytic activity. Experiments were also carried out in the presence of visible light in the reactor, without the usage of catalyst and it is observed that the dye solution cannot be decomposed by the light without the photocatalyst. This rules out the possibility of photolysis of the dye solution. Similarly the catalyst in dark cannot degrade the dye solution. Thus, the combination of light and catalyst is required for the degradation of methylene blue. This investigation also shows the importance of hydrogen peroxide in small amounts, which can enhance the catalytic activity. Almost, complete degradation is achieved using the 15% barium doped catalyst. The catalysts were separated by filtering after the treatment, further dried at room temperature. These were found to be stable during the photocatalytic treatment by powder XRD analysis (Supplementary Data, Fig. S1). The rate constants were calculated assuming pseudo-first order kinetics and details can be found in Supplementary Data (Table S2, Fig. S3-S6).

Conclusions

$BiVO_4$ was successfully synthesized as a single phase using solid state reactions. Bismuth sites were doped with barium and doped compounds were also prepared using the same method. Band gap of the parent compound was 2.19 eV and all the doped compounds exhibit band gaps which are closer to each other that indicate the insignificant effect of doping on band structure. Methylene blue was photodegraded by all the samples and their respective efficiencies were also estimated. 15% barium doped compound shows the highest activity among all, due to the smaller particle size. Reactions in sunlight show higher efficiencies and the addition of H_2O_2 plays a significant role in the photodegradation process. Complete decomposition of methylene blue is achieved by 15% barium doped $BiVO_4$ in the presence of sunlight along with small quantity of H_2O_2 which proves that the prepared catalyst is an effective one and further improvement of the catalyst can provide a promising material for the treatment of textile dyes.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_59A(06)775-782_SpplData.pdf.

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