

## Enhanced visible light assisted photo catalytic activity of $\text{Bi}_2\text{MO}_6$ (M=Mo, W) in presence of $\text{H}_2\text{O}_2$ for degradation of Rhodamine-B and Methylene blue

K. Deepthi<sup>1</sup>, P. Suresh<sup>2</sup>, A.M. Umabala<sup>1</sup>, A.V. Prasada Rao<sup>1</sup>

<sup>1</sup>*Dept. of Inorganic and Analytical Chemistry,  
Andhra University, Visakhapatnam, India.*

<sup>2</sup>*Dept. of Chemistry, JNTU-Kakinada, Kakinada, India.*

### Abstract

$\text{Bi}_2\text{WO}_6$  has been synthesized by solid-state metathesis reaction between  $\text{BiOCl}$  and  $\text{Na}_2\text{WO}_4$  at 600 °C. XRD and Raman spectroscopic studies indicated formation of mono phasic  $\text{Bi}_2\text{WO}_6$ . Phase pure  $\text{Bi}_2\text{MoO}_6$  could not be obtained under similar conditions by solid-state metathesis reaction between  $\text{BiOCl}$  and  $\text{Na}_2\text{MoO}_4$  because of its existence in three different phases  $\gamma$  (L),  $\gamma$  (H) and  $\gamma$  (I) corresponding to low temperature, high temperature and intermediate forms. Pure  $\gamma$ - $\text{Bi}_2\text{MoO}_6$  was obtained by co-precipitation method. Photocatalytic studies indicated that both Rhodamine-B and Methylene blue could be successfully degraded over  $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{MoO}_6$  under visible light irradiation. Presence of  $\text{H}_2\text{O}_2$  enhanced the rate of degradation due to a synergetic effect between  $\text{Bi}_2\text{WO}_6/\text{Bi}_2\text{MoO}_6$  and  $\text{H}_2\text{O}_2$ .

**Keywords:** Photocatalysis,  $\text{Bi}_2\text{MoO}_6$ ,  $\text{Bi}_2\text{WO}_6$ , Solid-state metathesis

### INTRODUCTION

Contamination of aquatic sources with waste water discharges from industries dealing with dyes, leather, paints, paper, pesticides, pharmaceuticals etc has become increasingly alarming since the remnant pollutants are often less biodegradable and are usually mutagenic or carcinogenic. Failure of conventional methods for effective decontamination of pollutants led to development of some new advanced oxidation

processes among which heterogeneous photo catalysis has been extensively studied over the past few decades. The process gained importance because a good number of soluble organic pollutants present in ppm range can be mineralized to non-toxic products more economically at ambient temperature avoiding filtration and secondary pollution.  $\text{TiO}_2$  has long been projected as a potential photo catalyst due to its ease of synthesis, chemical inertness, photo stability and easy availability. However, the wide band gap of  $\text{TiO}_2$  restricts its absorption only to U.V. region which is hardly  $< 4\%$  in solar radiation. In order to render the process energy efficient, there is a need to explore more efficient visible light active binary or ternary metal oxide photo catalysts. Several investigations in this regard revealed that Bi-based composite oxides such as  $\text{BiVO}_4$ ,  $\text{Bi}_2\text{O}_3 \cdot n \text{MoO}_3$  ( $n = 1, 2, 3$ ),  $\text{Bi}_2\text{WO}_6$ ,  $\text{Bi}_2\text{W}_3\text{O}_{12}$ ,  $\text{BiFeO}_3$ ,  $\text{NaBiO}_3$ ,  $\text{BaBiO}_3$  are promising because of their up shifted valance bands leading to smaller band gaps due to hybridization of 6s orbitals of Bi with 2p orbitals of oxygen. Out of these Bi-composite oxides,  $\text{Bi}_2\text{MO}_6$  ( $M = \text{Mo}, \text{W}$ ) exist as Aurivillius compounds of layered structure composed of  $(\text{Bi}_2\text{O}_2)^{2+}$  and  $\text{MO}_6$  octahedra which provides for migration of electrons and holes generated consequent to photo absorption. Ever since Shimodaira et al [1] reported the ability of Bi-molybdates to act as photo catalysts for  $\text{O}_2$  evolution from  $\text{AgNO}_3$  solution under visible light irradiation, and the reports of Kudo and Haji [2], Tang et al [3] and Zhang and Zhu [4] on the photo catalytic activity of  $\text{Bi}_2\text{WO}_6$ , interest in these oxides grew for their application as heterogeneous photo catalysts towards degradation of hazardous organic pollutants. Present paper describes visible light assisted photo catalytic degradation of Rhodamine-B and Methylene blue dyes using  $\text{Bi}_2\text{WO}_6$  synthesized by a new route involving solid-state metathesis and  $\text{Bi}_2\text{MoO}_6$  synthesized by conventional co-precipitation, with special reference to the effect of addition of  $\text{H}_2\text{O}_2$ , on the enhancement of catalytic efficiency.

## EXPERIMENTAL

### Materials and Methods:

$\text{Bi}_2\text{WO}_6$  is prepared by solid-state metathetic reaction between  $\text{BiOCl}$  and  $\text{Na}_2\text{WO}_4$  as precursors. Stoichiometric amounts of  $2\text{BiOCl}$  and  $\text{Na}_2\text{WO}_4$  are mixed and ground for 1 hr. The homogeneous mixture is subjected to heat treatment at  $600\text{ }^\circ\text{C}$  for 4 hrs, washed free from  $\text{Cl}^-$  at room temperature and dried.  $\text{Bi}_2\text{MoO}_6$  is prepared by co precipitation method using  $\text{Bi}(\text{NO}_3)_3$  and  $\text{Na}_2\text{MoO}_4$  following the procedure reported by Martinez-de la Cruz et al [5].

### Photocatalytic Studies:

100 mg of catalyst powder is added into 100 ml dye aqueous solution (10 mg/L) and

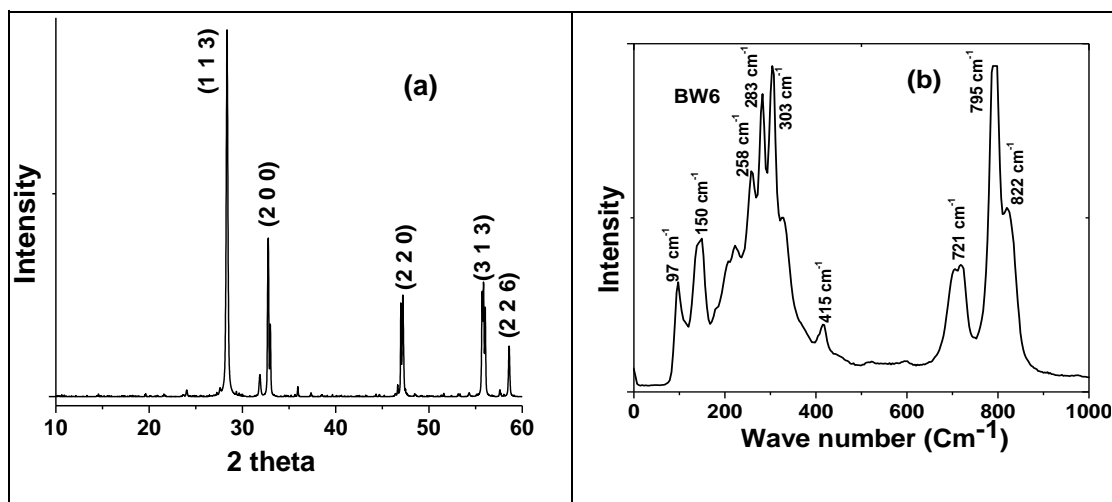
the suspension was magnetically stirred for half an hour in dark. The suspension is then exposed to 400 W metal halide lamp; 5 ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. Progress of decoloration is followed by recording the corresponding absorption spectra and the extent of photo catalytic degradation is obtained using the following equation.

$$\% \text{ Photo degradation} = [(A_t - A_0)/A_0] \times 100$$

where  $A_0$  and  $A_t$  correspond to initial absorbance and absorbance at time 't' respectively. All experiments have been performed at ambient conditions.

## **RESULTS AND DISCUSSION**

Solid-state metathesis offers a convenient route to synthesize mixed metal oxides at relatively lower temperatures compared to high temperature diffusion controlled ceramic oxide mixing method. Low temperature syntheses of several mixed metal oxides such as  $MWO_4$  (M= Mn, Fe, Co, Ni and Zn),  $BaSnO_3$ ,  $BaZrO_3$ ,  $BiFeO_3$ ,  $LaFeO_3$ ,  $BiVO_4$  by solid state metathesis have been reported from this laboratory [6-9]. Conventionally  $Bi_2WO_6$  is prepared by solid-state reaction between  $Bi_2O_3$  and  $WO_3$  at 900°C for 24 hrs. Syntheses of  $Bi_2WO_6$  has also been reported in terms of flux growth [11], wet chemical [12], ultrasonic [13], hydrothermal [14], solvothermal [15], micro wave hydrothermal [16], sol-gel [17], co-precipitation [18] and amorphous precursor [19] techniques. In the present study,  $Bi_2WO_6$  is prepared by solid-state metathesis. X-ray diffraction pattern of the homogenized ground mixture of  $2BiOCl + Na_2WO_4$  heat treated at 600°C for 4 hrs and washed with water and dried at 100 °C is shown in Fig 1(a). All the diffraction peaks observed in XRD pattern could be indexed to  $Bi_2WO_6$  of JCPDS File No 79-2381. Raman spectrum of the dried sample shown in Fig 1(b) was in good agreement with that of  $Bi_2WO_6$  literature reports [20]. Based on the XRD pattern and Raman spectral data, the resultant solid is therefore ascertained to be phase pure  $Bi_2WO_6$ .



**Fig. 1** XRD pattern (a) and Raman spectrum (b) of homogenized mixture of  $2\text{BiOCl} + \text{Na}_2\text{WO}_4$  heat treated at  $600\text{ }^\circ\text{C}$  for 4 h and washed free of chloride after cooling

When a similar attempt was made for the synthesis of  $\text{Bi}_2\text{MoO}_6$  starting from  $2\text{BiOCl} + \text{Na}_2\text{MoO}_4$ , XRD pattern of the ground mixture heat treated at  $600\text{ }^\circ\text{C}$  for 4 hrs did not indicate formation of phase pure  $\gamma\text{-Bi}_2\text{MoO}_6$  (Fig. 2a). XRD pattern of sample heat treated at  $700\text{ }^\circ\text{C}$  for 4 hrs showed the same pattern. Literature reports indicate that  $\gamma\text{-Bi}_2\text{MoO}_6$  can exist in three polymorphic forms  $\gamma\text{ (L)}$ ,  $\gamma\text{ (H)}$  and  $\gamma\text{ (I)}$  corresponding to low temperature form, high temperature form and an intermediate of high and low temperature forms respectively, of which  $\gamma\text{ (L)}$  and  $\gamma\text{ (H)}$  are stable forms, while  $\gamma\text{ (I)}$  is meta stable [21]. Based on thermo-Raman spectra, Muragan [22] suggested that the basic structure of  $\gamma\text{ (L)}$  was not dramatically disturbed from 25 to  $615\text{ }^\circ\text{C}$  and transition to  $\gamma\text{ (H)-Bi}_2\text{MoO}_6$  occurred at  $620\text{ }^\circ\text{C}$  with some subtle rearrangements in the structure occurring from  $500\text{ }^\circ\text{C}$  onwards. In view of this, heat treatment temperature is lowered and XRD patterns of ground mixture heat treated at  $550\text{ }^\circ\text{C}$  and  $450\text{ }^\circ\text{C}$  for 20 hrs are shown in the same figure (Fig. 2(b) and 2(c)). From the XRD patterns, it can be seen that formation of  $\gamma\text{ (L) Bi}_2\text{MoO}_6$  is evident for heat treatment at  $450\text{ }^\circ\text{C}$  for 20 hrs but the presence of some extra peaks suggest the product to be multi phasic consisting of both  $\gamma\text{ (L) Bi}_2\text{MoO}_6$  and  $\gamma\text{ (H) Bi}_2\text{MoO}_6$ .

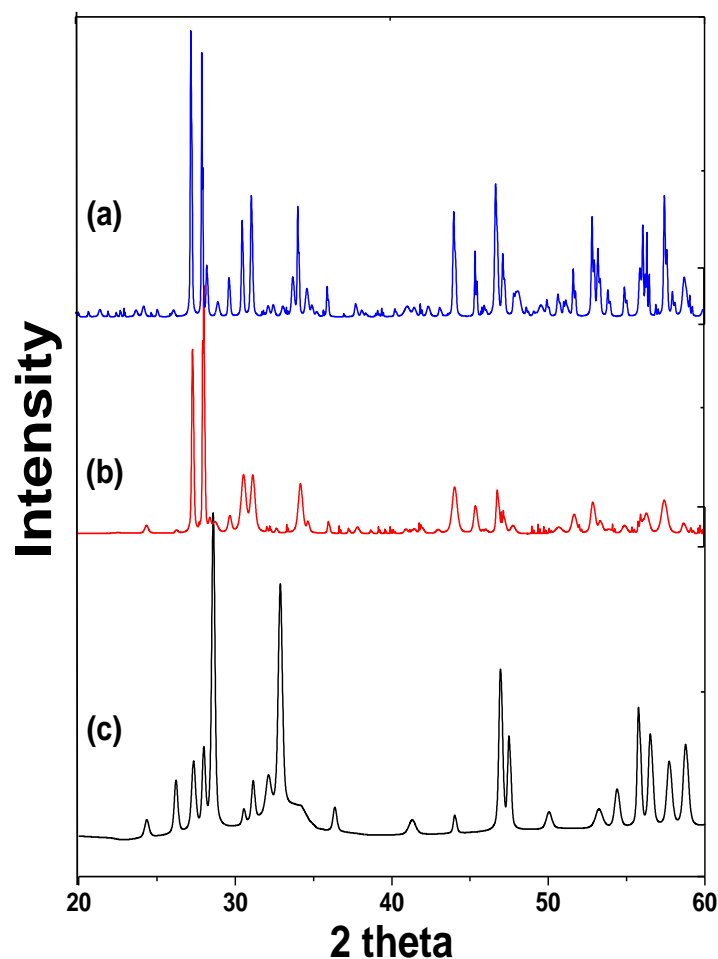
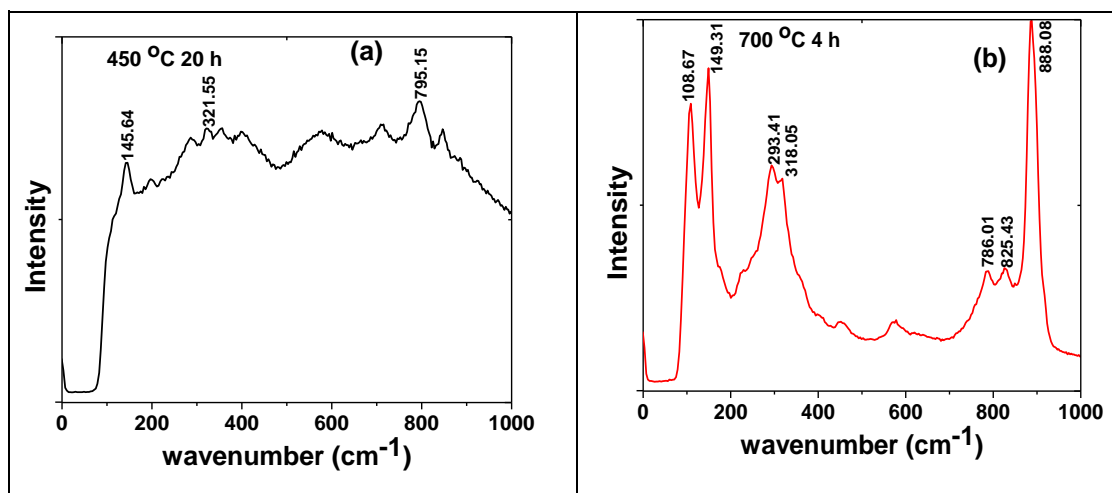


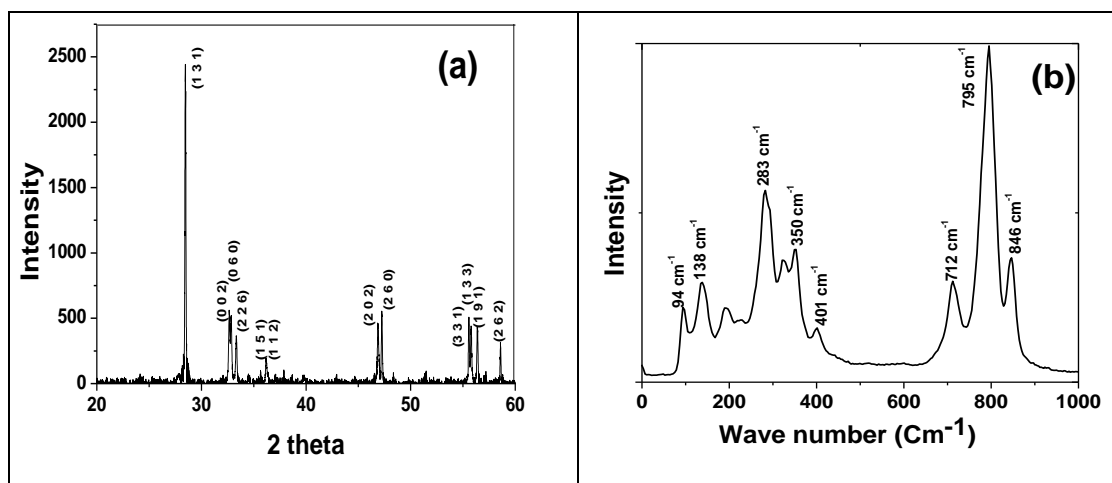
Fig. 2 XRD patterns of ground mixture of 2  $\text{BiOCl} + \text{Na}_2\text{MoO}_4$  powder heat treated at (a)  $600\text{ }^\circ\text{C}$  4 h, (b)  $550\text{ }^\circ\text{C}$  20 h and (c)  $450\text{ }^\circ\text{C}$  20 h (\* indicates  $\gamma\text{-Bi}_2\text{MoO}_6$  and washed free of chloride).

Raman spectra of the samples heat treated at  $450\text{ }^\circ\text{C}$  for 20 hrs and  $700\text{ }^\circ\text{C}$  for 4 hrs depicted in Fig. 3 are indicative of  $\gamma$  (L) as major phase and  $\gamma$  (H) as minor phase for low heat treatment temperature ( $450\text{ }^\circ\text{C}$ ),  $\gamma$  (H) and  $\gamma$  (L) as major and minor phases for high heat treatment temperature ( $700\text{ }^\circ\text{C}$ ) respectively based on literature reports [22]. Hence,  $\text{Bi}_2\text{MoO}_6$  is synthesized by co precipitation process. The precursor precipitate of  $\text{Bi}_2\text{MoO}_6$  is calcined at  $450\text{ }^\circ\text{C}$  for 20 hrs and the resultant powder is characterized by XRD and Raman



**Fig. 3** Raman spectra of homogenized ground mixture of  $2\text{BiOCl} + \text{Na}_2\text{MoO}_4$  heat treated at (a)  $450\text{ }^\circ\text{C}$  for 20 h and (b)  $700\text{ }^\circ\text{C}$  for 4 h, after being washed free from  $\text{Cl}^-$ .

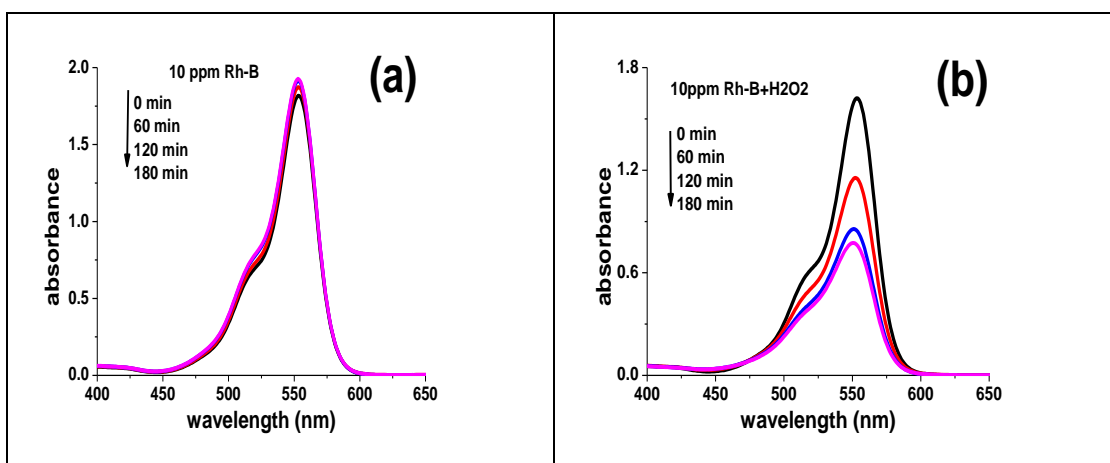
spectroscopic studies. All the observed peaks in the XRD pattern shown in Fig 4(a) are in good agreement with those reported for  $\gamma\text{-Bi}_2\text{MoO}_6$  of JCPDS File No 72-1524. In the Raman spectrum shown in Fig 4(b), the strong band at  $793\text{ cm}^{-1}$  is ascribed to symmetric stretching mode of  $\text{MoO}_6$  while the medium intensity peaks at  $712$  and  $840\text{ cm}^{-1}$  are assigned to asymmetric stretching mode. Peaks at  $323$ ,  $345$  and  $398\text{ cm}^{-1}$  are attributed to  $E_u$  symmetric bending, while peaks at  $290$  and  $280\text{ cm}^{-1}$  are correspond to  $E_g$  bending modes. Peaks below  $200\text{ cm}^{-1}$  are mainly due to lattice mode of  $\text{Bi}^{3+}$  perpendicular to layers.

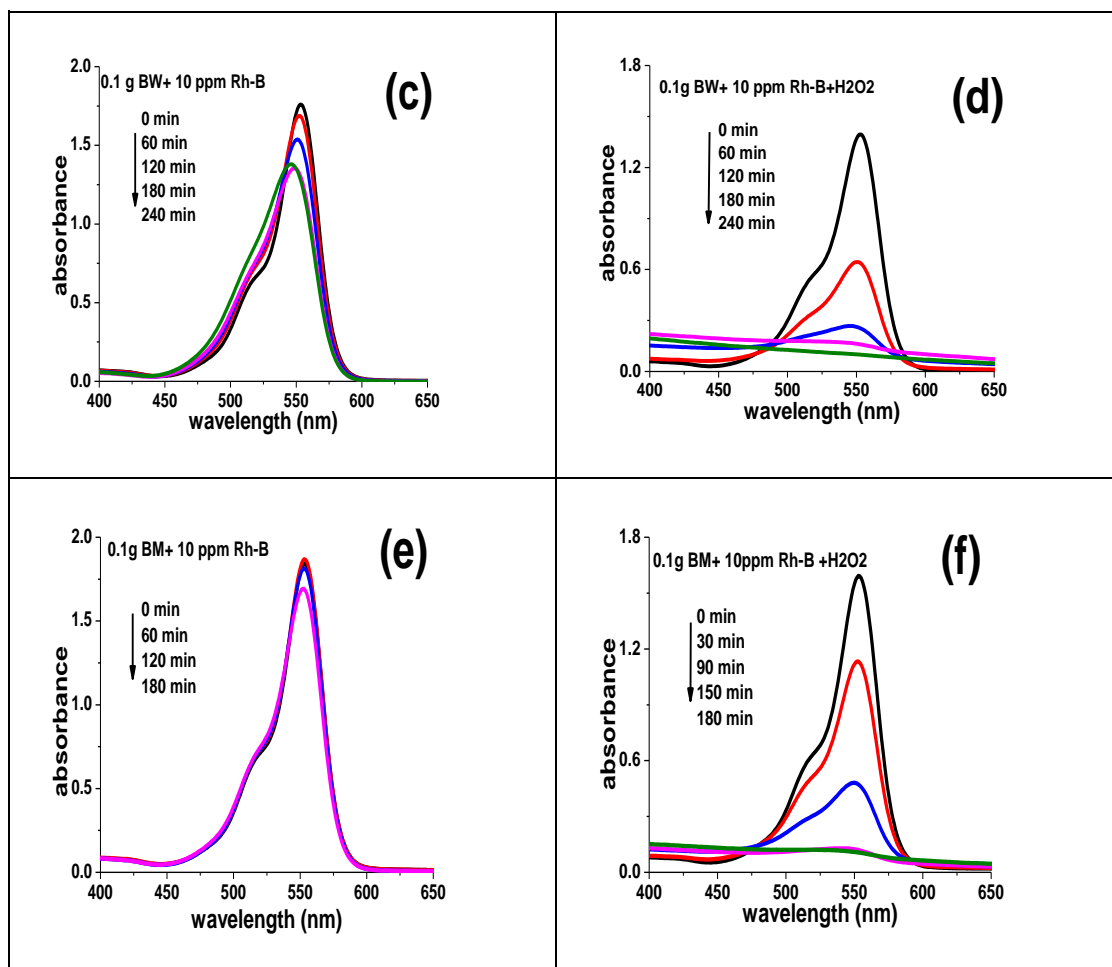


**Fig. 4** XRD pattern (a) and Raman spectrum (b) of  $\text{Bi}_2\text{MoO}_6$  precursor obtained by co-precipitation method and heat treated at  $450\text{ }^\circ\text{C}$  for 20 hrs.

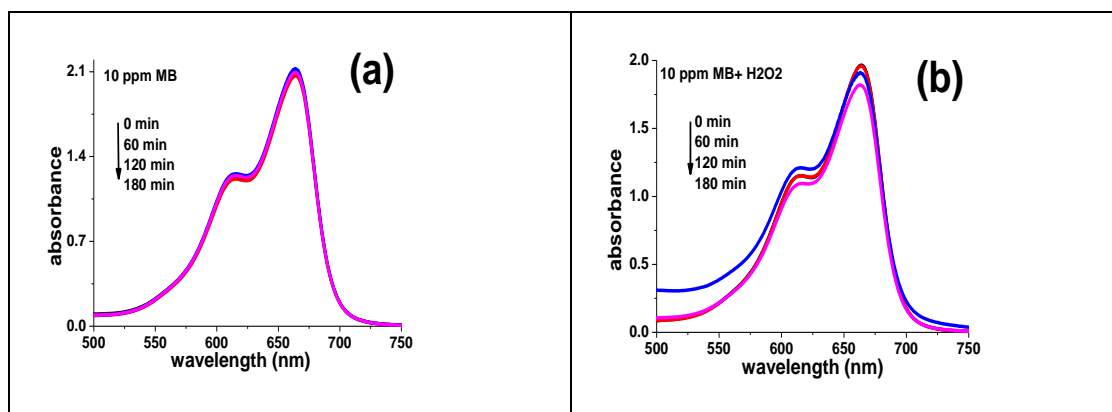
Photo catalytic degradation using nano  $\text{Bi}_2\text{WO}_6$  has been reported for Rhodamine-B [23, 24], Methylene blue [25, 26], Crystal violet [27, 28], Malachite green [29, 30] and Eosin-Y [31] while Photo catalytic degradation using nano  $\text{Bi}_2\text{MoO}_6$  has been reported for Rh-B [32-36], Methylene blue [32, 33, 35], Methyl orange [33, 34] and Carmine indigo [36]. Variation of spectral intensities as a function of irradiation time for Rhodamine-B (Rh-B), Rh-B+ $\text{H}_2\text{O}_2$ , Rh-B+ $\text{Bi}_2\text{WO}_6$ , Rh-B+ $\text{H}_2\text{O}_2$ + $\text{Bi}_2\text{WO}_6$ , Rh-B+ $\text{Bi}_2\text{MoO}_6$  and Rh-B+ $\text{H}_2\text{O}_2$ + $\text{Bi}_2\text{MoO}_6$  are shown in Fig. 5. From the figure, it can be seen that Rh-B has a characteristic absorption peak at  $\lambda_{\text{max}} = 550 \text{ nm}$  and does not show any photolysis for due to irradiation up to 180 min (Fig 5a). But, in presence of  $\text{H}_2\text{O}_2$ , Rh-B displays significant photo degradation to an extent of 50% for irradiation of 180 min (Fig 5b). In presence of  $\text{Bi}_2\text{WO}_6$ , Rh-B shows photo catalytic degradation to an extent of 28% (Fig 5c) for 180 min of irradiation. However, in presence of both  $\text{H}_2\text{O}_2$  and  $\text{Bi}_2\text{WO}_6$ , Rh-B is 93% decolorized for irradiation of 180 min (Fig 5d). In presence of  $\text{Bi}_2\text{MoO}_6$  alone, Rh-B shows photo degradation to an extent of 12% (Fig 5e) for 180 min of irradiation. But, in presence of both  $\text{H}_2\text{O}_2$  and  $\text{Bi}_2\text{MoO}_6$ , complete photo catalytic degradation of Rh-B is observed for 180 min of irradiation (Fig 5f). These results clearly suggest that the electron acceptor  $\text{H}_2\text{O}_2$  plays a significant role in enhancing the rate of photo catalytic degradation. Since photo catalytic degradation of Rh-B did not show any shift in wavelength of absorption maxima with progressive irradiation, degradation via successive deethylation can be ruled out.

Temporal variations of spectral intensities as a function of irradiation time for Methylene blue (MB), MB+ $\text{H}_2\text{O}_2$ , MB+ $\text{Bi}_2\text{WO}_6$ , MB+ $\text{H}_2\text{O}_2$ + $\text{Bi}_2\text{WO}_6$ , MB+ $\text{Bi}_2\text{MoO}_6$  and MB+ $\text{H}_2\text{O}_2$ + $\text{Bi}_2\text{MoO}_6$  are shown in Fig 6. From the figure, it is evident that MB shows a characteristic absorption with  $\lambda_{\text{max}} = 660 \text{ nm}$  and does not undergo any photolysis for

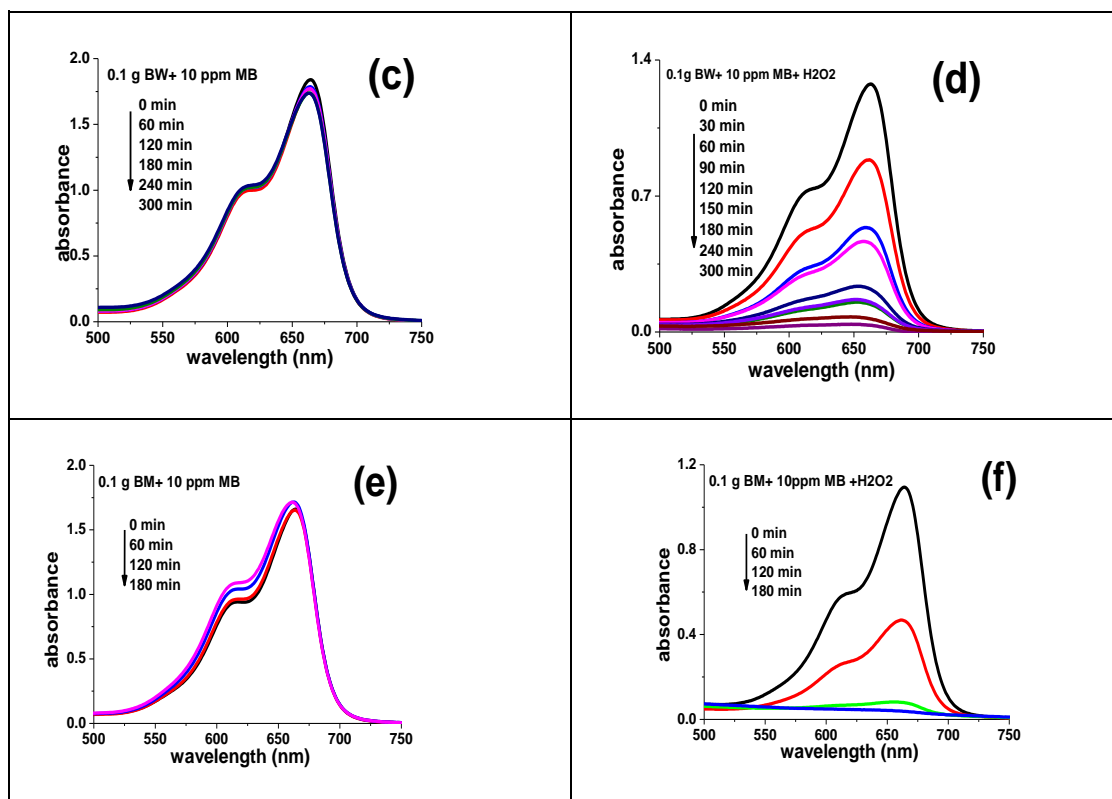




**Fig. 5** Variation of spectral contours as a function of irradiation time for (a) Rh-B, (b) Rh-B+H<sub>2</sub>O<sub>2</sub>, (c) Rh-B+Bi<sub>2</sub>WO<sub>6</sub>, (d) Rh-B+Bi<sub>2</sub>WO<sub>6</sub>+H<sub>2</sub>O<sub>2</sub>, (e) Rh-B+Bi<sub>2</sub>MoO<sub>6</sub> and (f) Rh-B+Bi<sub>2</sub>MoO<sub>6</sub>+H<sub>2</sub>O<sub>2</sub>.



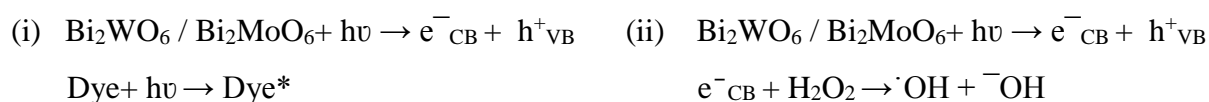


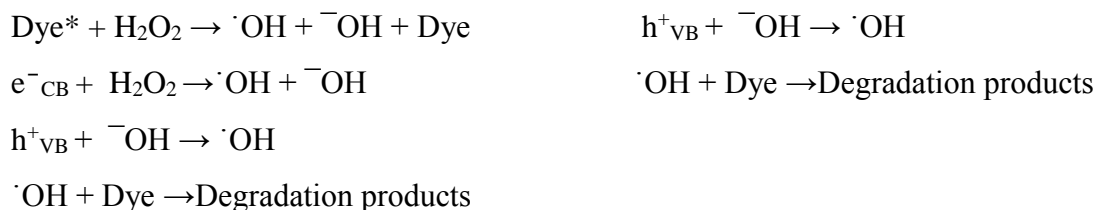


**Fig. 6.** Temporal variation of spectral intensities as a function of irradiation time for (a) MB, (b) MB+H<sub>2</sub>O<sub>2</sub>, (c) MB+Bi<sub>2</sub>WO<sub>6</sub>, (d) MB+Bi<sub>2</sub>WO<sub>6</sub>+H<sub>2</sub>O<sub>2</sub>, (e) MB+Bi<sub>2</sub>MoO<sub>6</sub> and (f) MB+Bi<sub>2</sub>MoO<sub>6</sub>+H<sub>2</sub>O<sub>2</sub>.

irradiation up to 180 min (Fig 6a). Unlike Rh-B, MB shows only 10% photo degradation for 180 min of irradiation in presence of H<sub>2</sub>O<sub>2</sub> (Fig 6b). In presence of Bi<sub>2</sub>WO<sub>6</sub>, MB displays negligible photo catalytic degradation even for 240 min of irradiation (Fig 6c). But in presence of H<sub>2</sub>O<sub>2</sub>+Bi<sub>2</sub>WO<sub>6</sub>, near complete decolorization of MB occurred for 240 min of irradiation (Fig 6d). Similarly in presence of Bi<sub>2</sub>MoO<sub>6</sub>, MB showed hardly 5% photo catalytic degradation (Fig 6e). But, in presence of both H<sub>2</sub>O<sub>2</sub> and Bi<sub>2</sub>MoO<sub>6</sub> complete decolorization of MB is achieved for 180 min of irradiation (Fig 6f).

The above results clearly indicate a synergetic effect between H<sub>2</sub>O<sub>2</sub> and Bi<sub>2</sub>WO<sub>6</sub>/Bi<sub>2</sub>MoO<sub>6</sub> in enhancing the rate of degradation. Based on these results, possible degradation mechanisms are suggested as follows. In case of Rh-B where photolysis is a dominant factor, the following mechanism (i) is likely. In case of MB where photocatalysis is dominant the following mechanism (ii) is likely.





## CONCLUSIONS

From the above studies, it may be concluded that phase pure  $\text{Bi}_2\text{WO}_6$  can be synthesized at lower temperature than ceramic method by solid state metathesis reaction between  $2\text{BiOCl}$  and  $\text{Na}_2\text{WO}_4$  at  $600\text{ }^\circ\text{C}$  for 4 hrs. Mono phasic  $\gamma\text{-Bi}_2\text{MoO}_6$  could not be obtained for heat treatment temperature in the range of  $400\text{-}700\text{ }^\circ\text{C}$  but phase pure  $\gamma\text{-Bi}_2\text{MoO}_6$  could be prepared by co-precipitation. Photo catalytic studies indicated that both Rhodamine-B and Methylene blue can be successfully degraded under visible light irradiation using  $\text{Bi}_2\text{WO}_6$  or  $\text{Bi}_2\text{MoO}_6$  in presence of  $\text{H}_2\text{O}_2$ . Synergetic effect between  $\text{H}_2\text{O}_2$  and  $\text{Bi}_2\text{MO}_6$  (M= W, Mo) led to rapid degradation of Rhodamine-B and Methylene blue dyes.

## REFERENCES

- [1]. Shimodaira, Y., Kato H, Kobayashi H, Kudo A., 2006, "Photophysical Properties and Photocatalytic Activities of Bismuth Molybdates under Visible Light Irradiation," *J. Phys. Chem. B.*, 110(36), 17790-17797.
- [2]. Zhang, Ch., Zhu, Y., 2005, "Synthesis of Square  $\text{Bi}_2\text{WO}_6$  Nanoplates as High-Activity Visible-Light-Driven Photocatalysts," *Chem. Mater.* 17(13), 3537-3545.
- [3]. Martinez-de la Cruz, A., Obregon Alfaro, S., 2010, "Synthesis and characterization of  $\gamma\text{-Bi}_2\text{MoO}_6$  prepared by co-precipitation: Photoassisted degradation of organic dyes under vis-irradiation," *J. Mol. Catal. A: Chem.*, 320(1-2), 85-91.
- [4]. Sujana Kumari, U., Suresh, P., Prasada Rao, AV., 2013, "Grinding assisted solid state metathetic synthesis of divalent transition metal tungstates," *Int. Res. J. Pure Appl. Chem.*, 3(1), 1-9.
- [5]. Sujana Kumari, U., Suresh, P., Prasada Rao, AV., 2013, "Solid state metathetic synthesis of phase pure  $\text{BaSnO}_3$  and  $\text{BaZrO}_3$ ," *Int. Res. J. Pure Appl. Chem.*, 3(4), 347-356.
- [6]. Sujana Kumari, U., Suresh, P., Prasada Rao, AV., 2013, "Solid state synthesis of  $\text{LaFeO}_3$  and  $\text{BiFeO}_3$  using  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  as precursors with La/Bi Chloride," *Int. J. Chem. Res.*, 2(2), 15-20.

- [7]. Sujana Kumari, U., Suresh, P., Prasada Rao, AV., 2014, "Room temperature solid state metathetic synthesis of photocatalytically active monoclinic BiVO<sub>4</sub> and tetragonal LaVO<sub>4</sub>," *J. Applicable Chem.*, 3(1), 366-371.
- [8]. Umabala, AM., Suresh, P., Prasada Rao, AV., 2016, "Effective visible light photocatalytic degradation of Brilliant green using H<sub>2</sub>O<sub>2</sub> sensitized BiVO<sub>4</sub>," *Derpharma chim.*, 8(1), 61-66.
- [9]. Yanovskii, VK., Voronkova, VI., 1986, Polymorphism and properties of Bi<sub>2</sub>WO<sub>6</sub> and Bi<sub>2</sub>MoO<sub>6</sub>," *Phys. Status Solidi. A.*, 93(1), 57-66.
- [10]. Kodols, M., Didrihsone, S., Grabis, J., 2013, "Preparation of nanosized bismuth tungstate and its photocatalytic activity", *CYSENI 2013*, May 29-31, Kaunas, Lithuania.
- [11]. Zhou, L., Wang, W., Zhang, L., 2007, "Ultrasonic-assisted synthesis of visible-light-induced Bi<sub>2</sub>MO<sub>6</sub> (M = W, Mo) photocatalysts," *J. Mol. Catal. A: Chem.*, 268(1-2), 195-200.
- [12]. Shang, M., Wang, W., Zhaang, L., Xu, H., 2010, "Bi<sub>2</sub>WO<sub>6</sub> with significantly enhanced photocatalytic activities by nitrogen doping," *Mater. Chem. Phys.*, 120(1), 155-159.
- [13]. Gui, MS., Zhang, WD., Su, QX., Chen, CH., 2011, "Preparation and visible light photocatalytic activity of Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> heterojunction photocatalysts," *J. Solid state Chem.*, 184(8), 1977-1982.
- [14]. Xie, H., Shen, D., Wang, X., Shen, G., 2007, "Microwave hydrothermal synthesis and visible-light photocatalytic activity of Bi<sub>2</sub>WO<sub>6</sub> nanoplates," *Mater. Chem. Phys.*, 103(2-3), 334-339.
- [15]. Zhang, G., Lu, F., Li, M., Yang, J., Zhang, X., Huang, B., 2010, "Synthesis of nanometer Bi<sub>2</sub>WO<sub>6</sub> synthesized by sol-gel method and its visible-light photocatalytic activity for degradation of 4BS," *J. Phys. Chem. Solids.*, 71(4), 579-582.
- [16]. Obregon Alfaro, S., Martinez-de la Cruz, A., 2010, "Synthesis, characterization and visible-light photocatalytic properties of Bi<sub>2</sub>WO<sub>6</sub> and Bi<sub>2</sub>W<sub>2</sub>O<sub>9</sub> obtained by co-precipitation method," *J. Appl. Catal. A: Gen.*, 383(1-2), 128-133.
- [17]. Zhang, S., Zhang, Ch., Man, Y., Zhu, Y., 2006, "Visible-light-driven photocatalyst of Bi<sub>2</sub>WO<sub>6</sub> nanoparticles prepared via amorphous complex precursor and photocatalytic properties," *J. Solid State Chem.*, 179(1), 62-69.
- [18]. Phuruangrat, A., Ekthammathat, N., Kuntalu, B., Thongtem, T., 2014, "Hydrothermal Synthesis, Characterization, and Optical Properties of Ce

- Doped  $\text{Bi}_2\text{MoO}_6$  Nanoplates,” *J. Nanomater.*, DOI: 10.1155/2014/934165.
- [19]. Murugan, R., Ghule, A., Chang, H., 2000, “Thermo-Raman spectroscopic studies on polymorphism in  $\text{Na}_2\text{SO}_4$ ,” *J. Phys: Cond. Matter.*, 12(5), 677.
- [20]. Murugan, R., Gangadharan, R., Kalaiselvi, J., Sukumar, S., Palanivel, B., Mohan, S., 2002, “Investigation of structural changes in the phase transformations of  $\gamma\text{-Bi}_2\text{MoO}_6$ ,” *J. Phys. Cond. Matter.*, 14, 4001.
- [21]. Dumrongrojthanath, P., Thongtem, T., Phuruangrat, A., Thongtem, S., 2013, “Hydrothermal synthesis of  $\text{Bi}_2\text{WO}_6$  hierarchical flowers with their photonic and photocatalytic properties,” *Super latt. Microstruc.*, 54, 71-77.
- [22]. Shan, G., Fu, Y., Chu, X., Chng, Ch., Zhu, L., 2015, “Highly active magnetic bismuth tungstate/magnetite composite under visible light irradiation in the presence of hydrogen peroxide,” *J. Colloid Inter. Sci.*, 444, 123-131.
- [23]. Ahsaine, HA., Taoufyq, A., Ezahri, Md., Benlhachemi, A., Gavarri, JR., 2013, 13th International Symposium on Nondestructive Characterization of Materials (NDCM-XIII), May, 20-24, Le Mans, France, (2013).
- [24]. Cui, Y., Li, H., Hong, W., Fan, S., Zhu, L., 2013, “The effect of carbon content on the structure and photocatalytic activity of nano- $\text{Bi}_2\text{WO}_6$  powder,” *Powder Technol.*, 247, 151-160.
- [25]. William Lee, WL., Huang, ST., Chang, JL., Chen, JY., Cheng, MC., Chen, CC., 2012, “Photodegradation of CV over nanocrystalline bismuth tungstate prepared by hydrothermal synthesis,” *J. Mol. Catal. A: Chem.*, 361, 80-90.
- [26]. Ben Liao, YH., Wang, JX., Lin, JS., Chung, WH., Lin, WY., Chen, CC., 2011, “Synthesis, photocatalytic activities and degradation mechanism of  $\text{Bi}_2\text{WO}_6$  toward crystal violet dye” *Catal. Today.*, 174, 148-159.
- [27]. Chen. Y., Zhang, Y., Liu, Ch., Lu, A., Zhang, W., 2012, “Photodegradation of Malachite Green by Nanostructured  $\text{Bi}_2\text{WO}_6$  Visible Light-Induced Photocatalyst,” *Int. J. Photoenergy.*, doi. org / 10.1155 / 510158.
- [28]. Ju, Y., Hong, J., Zhang, X., Xu, Z., Wei, D., Sang, Y., Fang, X., Fang, J., 2012, “Synthesis of surface sulfated  $\text{Bi}_2\text{WO}_6$  with enhanced photocatalytic performance,” *J. Environ. Sci.*, 24(12), 2180-2190.
- [29]. Hu, T., Li, H., Zhang, R., Du, N., Hou, W., 2016, “Thickness-determined photocatalytic performance of bismuth tungstate nanosheets,” *RSC Adv.*, 6, 31744-31750.
- [30]. Zha, X., Xu, T., Yao, W., Zhu, Y., 2009, “Photodegradation of dye pollutants catalyzed by  $\gamma\text{-Bi}_2\text{MoO}_6$  nanoplate under visible light irradiation,” *Appl. Surf. Sci.*, 255(18), 8036-8040.

- [31]. Yuan, B., Wang, C., Qi, Y., Song, X., Mu, K., Guo, P., Meng, L., Xi, H., 2013, "Decorating hierarchical Bi<sub>2</sub>MoO<sub>6</sub> microspheres with uniformly dispersed ultrafine Ag nanoparticles by an in situ reduction process for enhanced visible light-induced photocatalysis," *Colloids Surf. A.*, 425, 99-107.
- [32]. Li, J., Liu, X., Sun, Z., Sun, Y., Pan, L., 2015, "Novel yolk-shell structure bismuth-rich bismuth molybdate microspheres for enhanced visible light photocatalysis," *J. Colloid. Inter. Sci.*, 452, 109-115.
- [33]. Sun, Y., Wang, W., Sun, S., Zhang, L., 2013, "A general synthesis strategy for one-dimensional Bi<sub>2</sub>MO<sub>6</sub> (M = Mo, W) photocatalysts using an electrospinning method," *Cryst. Eng. Comm.*, 15, 7959-7964.
- [34]. Martinez-de la Cruz, A., Obregon Alfaro, S., 2010, "Synthesis and characterization of  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> prepared by co-precipitation: Photoassisted degradation of organic dyes under vis-irradiation," *J. Mol. Catal. A: Chem.*, 320(1-2), 85-91.

