

Visible Light Assisted Photocatalytic Degradation of Methyl Orange and Congo Red Using Bi_2WO_6 Prepared by Solid-State Metathesis

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Received: 26 October 2017;

Accepted: 31 January 2018;

Published online: 29 March 2018;

AJC-18828

Bi_2WO_6 a visible light photocatalyst is synthesized by solid-state metathesis reaction between BiOCl and Na_2WO_4 as precursors. X-ray diffraction pattern of ground homogenized mixture of precursors heat treated at 600 °C for 4 h and washed free from byproduct NaCl indicated formation of phase pure Bi_2WO_6 . Photocatalytic activity of Bi_2WO_6 powder is evaluated in terms of photocatalytic degradation of methyl orange and congo red under visible light irradiation, presence of external oxidant is found enhance the rate of degradation in both cases. Formation of $\cdot\text{OH}$ free radicals during irradiation is ascertained through scavenger D-manitol.

Keywords: Bi_2WO_6 , Photocatalytic degradation, Solid-state metathesis, Methyl orange, Congo red, D-Manitol.

INTRODUCTION

There has been a growing interest in the remediation of organic pollutants from industrial waste water exhausts based on semiconductor mediated heterogeneous photocatalysis. Interest in this technique is sustained because several organic pollutants can be oxidized non-selectively at ambient temperature without formation of any hazardous intermediates. Titanium dioxide (TiO_2) is the widely studied and extensively used photocatalyst because it is inexpensive, easy to synthesize, chemically inert and non-photodegradable. Nevertheless, the wide band gap associated with TiO_2 allows photo absorption only in the UV region which constitutes < 5 % in solar radiation, rendering the process energy constrictive. Though TiO_2 can be transformed into a visible light active photocatalyst by means of suitable doping with transition metal atoms, anions and cations, the enhanced photocatalytic efficiency is limited in terms of an optimal concentration of dopants because excess dopant concentration causes dopants as recombination centres for photo generated e^- and h^+ and becomes detrimental. Alternately, a number of binary metal oxides Fe_2O_3 , WO_3 , Cu_2O and ternary metal oxides ZnWO_4 , BiVO_4 , BiFeO_3 , $\text{Zn}_3(\text{VO}_4)_2$, Bi_2MoO_6 , $\text{Bi}_2\text{Mo}_2\text{O}_9$, $\text{Bi}_2\text{Mo}_3\text{O}_{12}$, Bi_2WO_6 , $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, NaBiO_3 have been explored as visible light active photocatalysts to exploit the available 50-55 % visible region of solar radiation in place of UV light for photogeneration of electrons and holes

[1]. Among the various ternary mixed metal oxides that are investigated, bismuth based oxides seem to be good candidates because of their band gaps that are active in the visible range, besides being chemically and thermally stable and non-toxic. Bismuth mixed oxides form an important set of visible light active photocatalysts called Aurivillius compounds respected by the general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ where $\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Bi}, \text{Pb}, \text{Na}, \text{K}$ and $\text{B} = \text{Ti}, \text{Nb}, \text{Ta}, \text{W}, \text{Mo}, \text{Fe}$. These are layered compounds consisting of perovskite slabs of $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ sandwiched between $(\text{Bi}_2\text{O}_2)^{2+}$ layers. Bi_2WO_6 is a typical Aurivillius compound with $n=1$, $\text{A} = \text{Bi}$, $\text{B} = \text{W}$. Bi_2WO_6 is known to be a high T_c ferro electric material [2], a high density phosphor [3], a gas sensor sensitive to alcohol [4], a solid-state ionic conductor [5] as well as a good n-type semiconductor photocatalyst with a narrow band gap in the region 2.6 to 2.8 eV [6]. Visible light assisted photocatalytic degradation of rhodamine-B [7,8], methylene blue [9,10], crystal violet [11,12], malachite green [13,14] and eosin-Y [15] have been reported with Bi_2WO_6 .

Synthesis of Bi_2WO_6 has been reported in terms of solid-state reaction [9], flux growth [16], wet chemical [17], ultrasonic [18], hydrothermal [19-22], solvothermal [23], microwave-hydrothermal [24], sol-gel [25], coprecipitation [26] and amorphous precursor [27] methods. Synthesis of several mixed metal oxides such as MWO_4 , BiFeO_3 and BiVO_4 have been reported from this laboratory in terms of solid-state metathesis reactions [28-30]. Present paper describes solid-state meta-

thetic synthesis, characterization and photocatalytic evaluation of Bi₂WO₆ for the degradation of methyl orange and congo red dyes.

EXPERIMENTAL

Synthesis of photocatalyst: Stoichiometric amounts of BiOCl and Na₂WO₄ as per the following reaction:



have been mixed and ground in an agate mortar for 2 h. The ground homogenized mixture is subjected to heat treatment at 500 °C and 600 °C for 4 h. The resultant mixture is washed with water until it is free from Cl⁻, dried in an air oven and subjected to X-ray diffraction for phase identification and phase purity. Micro structure relating to particle size and texture is investigated by scanning electron microscopy.

Photocatalytic studies: Photocatalytic activity of Bi₂WO₆ is evaluated in terms of degradation of methyl orange and congo red under visible light. 100 mg of the catalyst is dispersed in 100 mL methyl orange/congo red aqueous solution (10 mg/L) and the suspension is magnetically stirred for 0.5 h in dark to ensure adsorption/desorption equilibrium between photocatalyst powder and dye solution. The suspension is then exposed to 400 wt metal halide lamp; 5 mL aliquots are pipetted at periodic time intervals and filtered through 0.45 μ Millipore filters to remove any suspended powder. The spectra as a function of irradiation time are recorded using UV-visible spectrophotometer (Shimadzu). The extent of photodegradation is calculated using the following equation:

$$\text{Photodegradation (\%)} = \frac{(A_0 - A_t)}{A_0} \times 100$$

where A₀ and A_t correspond to initial absorbance and absorbance at time 't' respectively.

RESULTS AND DISCUSSION

Fig. 1 depicts X-ray diffraction (XRD) patterns of homogenized ground mixture of BiOCl and Na₂WO₄ subjected to heat treatment for 4 h at 500 and 600 °C. XRD pattern corresponding to 500 °C heat treatment showed a number of peaks characteristic of both precursors indicating that the solid-state reaction is not complete. However, XRD pattern of sample heat treated at 600 °C for 4 h showed sharp peaks corresponding to Bi₂WO₆ of JCPDS file No. 79-2381. In the absence of any unindexed peaks, the sample is ascertained to be phase pure Bi₂WO₆. SEM micro graph shown in Fig. 2 revealed the particle size in μm region with no characteristic morphology.

Temporal variation of spectral contours as a function of irradiation time for methyl orange (MO), MO + H₂O₂, MO + Bi₂WO₆ and MO + Bi₂WO₆ + H₂O₂ are shown in Fig. 3. From the figure it can be seen that methyl orange shows characteristic absorption at λ = 460 nm and irradiation up to 120 min did not cause any photolysis (Fig. 3a). In presence of H₂O₂ also, methyl orange did not show any photodegradation for irradiation up to 120 min (Fig. 3b). In presence of Bi₂WO₆, there is a slight increase in intensity, probably due to initial adsorption and subsequent desorption followed by irradiation (Fig. 3c). However, in presence of both Bi₂WO₆ and H₂O₂, the

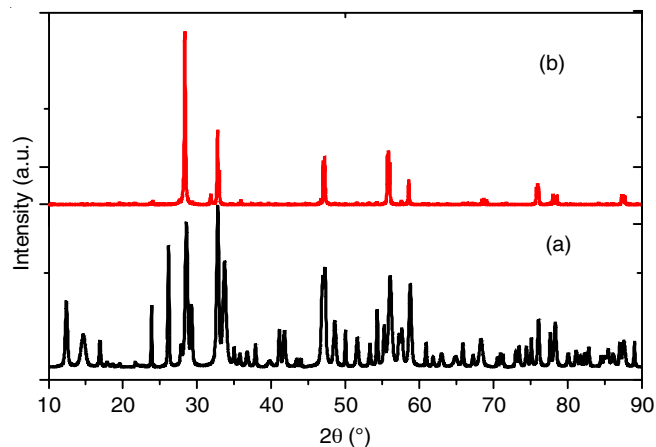


Fig. 1. XRD pattern of ground mixture of BiOCl + Na₂WO₄ heat treated at (a) 500 °C and (b) 600 °C for 4 h and washed with water

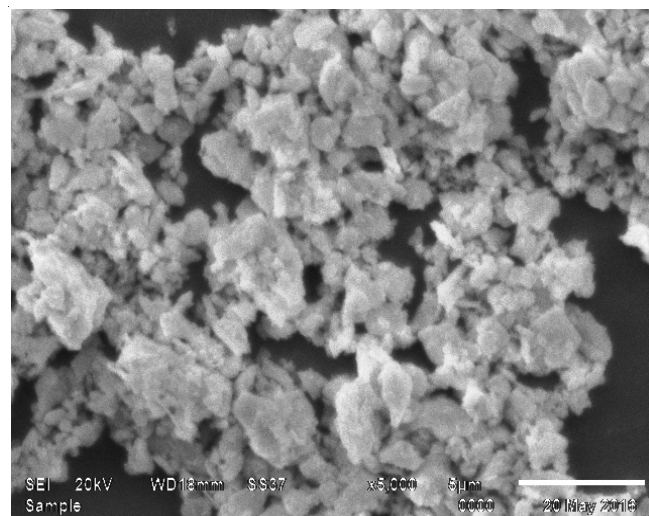


Fig. 2. SEM micrograph of sample heat treated at 600 °C and washed with water

intensity gradually decreased with progressive irradiation and nearly 87 % of methyl orange is photo catalytically degraded (Fig. 3d) for irradiation of 180 min. Kim and coworkers [31] reported the photocatalytic degradation of methyl orange using hydrothermally synthesized Bi₂WO₆ and calcined at 600 °C. According to these investigators 5 ppm methyl orange was completely photo catalytically degraded for 4 h of UV irradiation. Tian *et al.* [20] reported photocatalytic degradation of methyl orange using hydrothermally synthesized C₃N₄-Bi₂WO₆ under visible light irradiation for 120 min and concluded that O₂^{•-} was the active species for degradation. Yu-Min and Wen-Shan [32] investigated the photocatalytic degradation of methyl orange over Bi₂WO₆ and BiOI/Bi₂WO₆. According to these investigators Bi₂WO₆ photo degraded methyl orange to an extent of 50 % under UV irradiation and 21.5 % under visible light irradiation and the photo degradation enhanced to 98 % under UV and 87 % under visible light irradiation with BiOI/Bi₂WO₆. In the present study photo degradation of methyl orange is achieved in 180 min with pure Bi₂WO₆ under visible light irradiation with addition of external oxidant H₂O₂ only.

Time dependent variation of spectral intensities as a function of irradiation time for congo red (CR), CR + H₂O₂, CR + Bi₂WO₆ and CR + Bi₂WO₆ + H₂O₂ are shown in Fig. 4. From

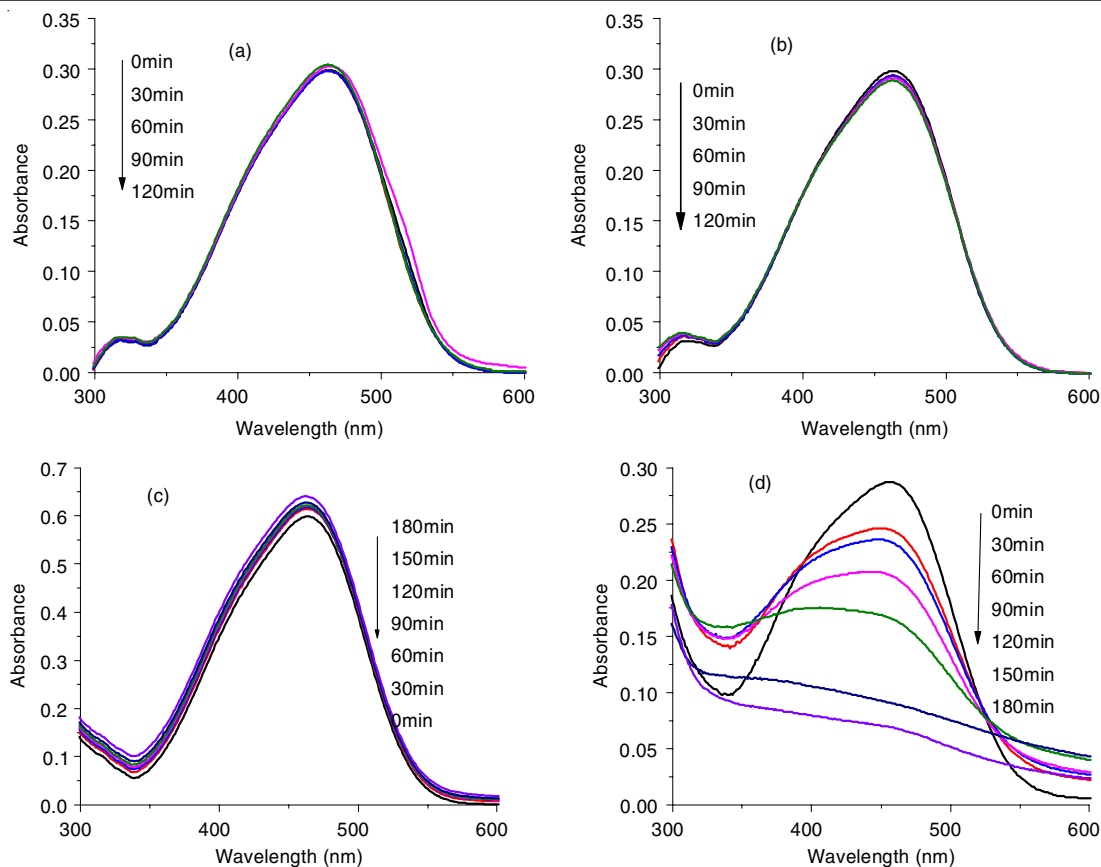


Fig. 3. Temporal variation of spectral contours as a function of irradiation time for (a) methyl orange, (b) MO + H₂O₂, (c) MO + Bi₂WO₆ and (d) MO + Bi₂WO₆ + H₂O₂

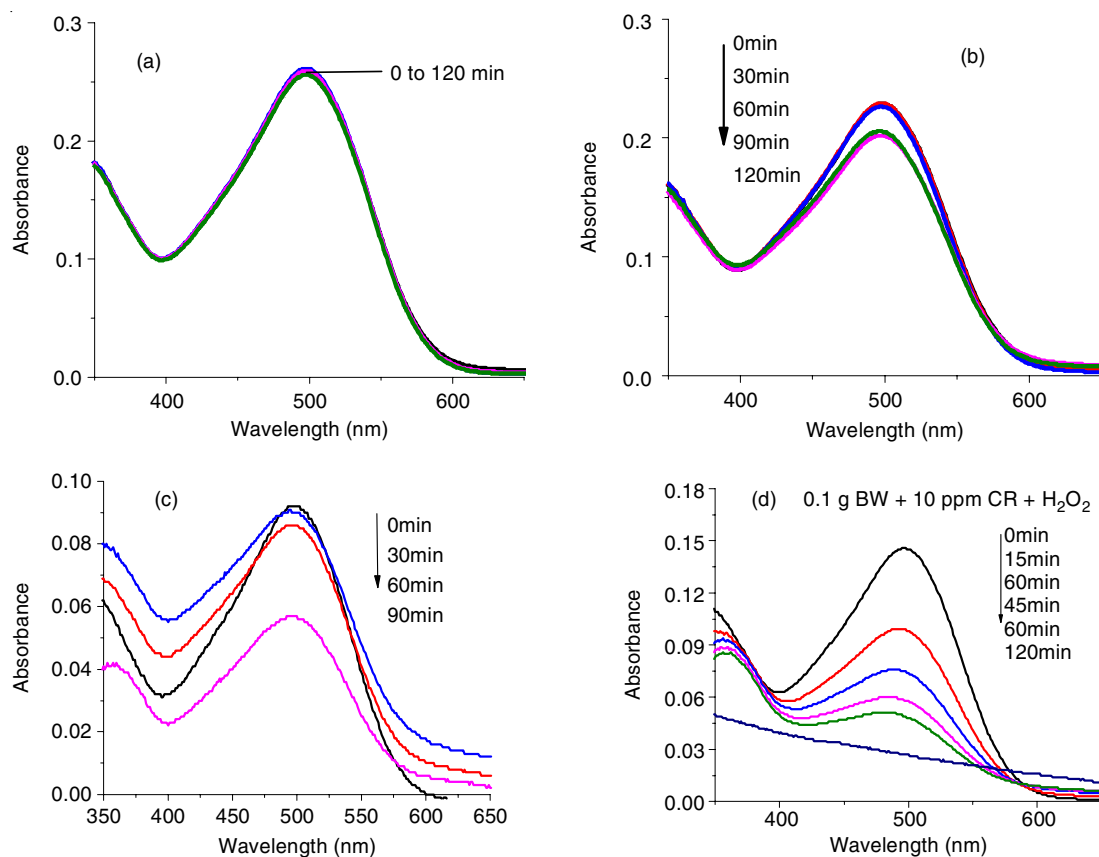


Fig. 4. Variation of spectral intensities as a function of irradiation time for (a) congo red, (b) CR + H₂O₂, (c) CR + Bi₂WO₆ and (d) CR + Bi₂WO₆ + H₂O₂

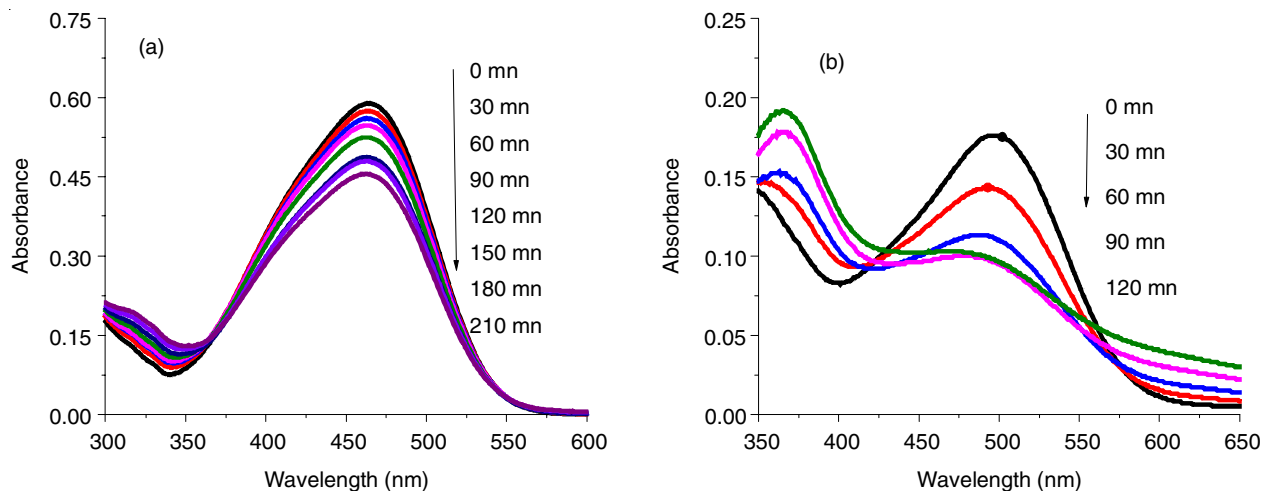


Fig. 5. Effect of D-manitol on photocatalytic degradation of (a) methyl orange and (b) congo red as a function of irradiation time (10 ppm dye + 100 mg Bi_2WO_6 + 10 μmol H_2O_2)

the figure, it can be seen that congo red exhibits a characteristic absorption at $\lambda = 490$ nm and did not show any photolysis even after irradiation for 120 min (Fig. 4a). In presence of H_2O_2 , there is hardly 10 % photo degradation for irradiation of 120 min (Fig. 4b). In presence of Bi_2WO_6 , congo red has undergone 40 % photo degradation for irradiation of 90 min (Fig. 4c). However, in presence of both Bi_2WO_6 and H_2O_2 , photo degradation to an extent of 70 % has occurred (Fig. 4d). These results indicate that Bi_2WO_6 and H_2O_2 exhibit a synergetic effect to enhance the photo degradation of congo red.

In order to assess the role of external oxidant H_2O_2 in the photocatalytic degradation of either methyl orange or congo red, the respective degradation studies are performed in presence of D-manitol. Corresponding spectral variations as a function of irradiation time are shown in Fig. 5. Both spectra indicate higher degradation times compared to degradation times observed without D-manitol. Since D-manitol is known to be a scavenger for $\cdot\text{OH}$ free radicals the degradation slowed down in presence of D-manitol.

Conclusion

The above results conclude that the phase pure Bi_2WO_6 can be synthesized using solid-state metathetic reaction between BiOCl and Na_2WO_4 at 600 $^\circ\text{C}$ for 4 h. Bi_2WO_6 photocatalytically degraded methyl orange and congo red for 180 and 120 min of visible light irradiation. Addition of H_2O_2 showed a synergetic effect in enhancing rate of photocatalytic degradation in both cases. Addition of D-manitol increased photocatalytic degradation time indicating scavenging effect on $\cdot\text{OH}$ free radicals formed during irradiation.

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