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Photocatalytic degradation of Brilliant Green, Carmine Indigo and Toluidine Blue using H₂O₂ sensitized Bi₂WO₆ and visible light

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ABSTRACT

Visible light activated photocatalytic degradations of Brilliant green, Carmine indigo and Toluidine blue dyes have been studied using Bi₂WO₆ synthesised by solid-state metathesis. Complete degradation of the above dyes is achieved for 240, 135 and 75 min of irradiation respectively. Addition of external oxidant H₂O₂ enhanced the rate of degradation and formation of ·OH free radicals during irradiation in presence of H₂O₂ is established by photoluminescence studies using terphthalic acid as probe molecule.

Key words: Bi₂WO₆, Brilliant green, Carmine indigo, Toluidine blue, Photocatalysis.

INTRODUCTION

Semiconductor mediated heterogeneous photocatalytic degradation offers distinct advantages over conventional methods for the remediation of toxic organic pollutants at very low concentrations in ppm range. The process is amenable at ambient temperature, does not generate hazardous intermediates, cost effective when visible region of solar radiation is used and environmental friendly. Recent literature survey indicates the projection of several ternary metal oxides that include ZnWO₄, BiVO₄, Bi₂Mo₃O₁₂, Fe₂Mo₃O₁₂, Bi₂WO₆, Bi₂MoO₆, and NaBiO₃ as potential visible light active photocatalysts [1].

Brilliant Green (BG), a triphenyl methane dye is extensively used for dyeing nylon, wool, cotton, and silk in textile industries as well as for colouring of oils, fats, waxes, plastic and varnishes. BG is highly toxic and causes irritation of respiration and gastrointestinal tract leading to vomiting and diarrhoea. It is banned in many countries because of its carcinogenic nature. Photocatalytic degradation of BG was reported by Ankit Kumar Jain and co-workers [2] over N, S co doped TiO₂, Hae Soo Park and Weon Bee Ko [3] over Nb₂O₅-graphene nanocomposites, Sudha Subrhamaniyan [4] over CeO₂-(NaX) Zeolite, Chen et al [5] over TiO₂, Swati Sood et al [6] over Sr doped TiO₂, Dong et al [7] over TiO₂-SiO₂ mesoporous nanocomposite, Shanmugam et al [8] over doped SnO₂, Ragupathy and coworkers [9] over TiO₂ nanoparticles on activated carbon and Umabala et al [10] over BiVO₄.

Carmine indigo (CI) is an anionic dye. Photocatalytic degradation of CI was reported using TiO₂ and H₂O₂ [11], TiO₂/UV/O₂ & H₂O₂ [12], TiO₂ impregnated active carbon [13], TiO₂ coated non-oven fibres [14], γ-Bi₂MoO₆ [15], ZnO [16], Sm₂FeTaO₇ impregnated with CuO [17], N-doped TiO₂ [18], Bi₂Mo₃O₁₂ [19] and Fe₂Mo₃O₁₂ [20].

Toluidine blue (TB) is a phenothiazine type dye used in textile industry and was reported to exert mutagenic and toxic interaction with DNA and RNA. Photocatalytic degradation of TB was reported using TiO₂ [21], ZnO [22], V₂O₅ thin film [23], SnO₂/V₂O₅ nano wires [24], MoO₃ and Cu_{0.33} MoO₃ [25], CdS [26], MoO₃-MWCNT nano composites [27], SnO₂ coated PZT [28], LaFeO₃ [29] and Mo-TiO₂ [30].

Bi₂WO₆ is an Aurivillius type compound with layered structure. It is an n-type semiconductor with a band gap in the range of 2.6 to 2.8 eV. Bi₂WO₆ has been reported to be a good visible light active photocatalyst for the degradation

of Rhodamine-B, Methylene blue, Crystal violet, Malachite green, and Eosin-Y [31-36]. Present paper describes photocatalytic degradation of Brilliant green, Carmine indigo and Toluidine blue using H₂O₂ sensitized Bi₂WO₆ and visible light.

MATERIALS AND METHODS

Bi₂WO₆ is prepared using solid-state metathetic reaction between BiOCl and Na₂WO₄ as precursors. Stoichiometric amounts of BiOCl and Na₂WO₄ are mixed and ground for 1 hrs. The homogeneous mixture is heated to 600°C for 4 hrs. After cooling, the mixture is thoroughly washed with water to remove the byproduct NaCl and the sample is subjected to X-ray diffraction studies for phase identification using Nickel filtered Cu-K_α radiation ($\lambda = 1.54059 \text{ \AA}$), with a scan rate of 4° min⁻¹.

Photocatalytic studies:

Photocatalytic activity of Bi₂WO₆ is evaluated in terms of degradation of Brilliant green, Carmine indigo and Toluidine blue under visible light. 100 mg of the catalyst is dispersed in 100 ml Brilliant green (10 ppm)/ Carmine indigo (20 ppm)/ Toluidine blue (10 ppm) aqueous solution and the suspension is magnetically stirred for half an hour in dark to ensure adsorption/desorption equilibrium between photocatalyst powder and dye solution. The suspension is then exposed to 400 W metal halide lamp; 5ml aliquots are pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove any suspended powder. The spectra as a function of irradiation time are recorded using UV-Visible spectrophotometer (Schimadzu). The extent of photo degradation is calculated using the following equation

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

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

Photoluminescence studies:

50 mg Bi₂WO₆ catalyst is added to the beaker containing 100 ml of terphthalic acid (TPA) solution (0.25 mmol L⁻¹ in 1mmol L⁻¹ NaOH solution) and 10 μmol H₂O₂. The solution is stirred for 30 min in dark followed by irradiation by 400 W metal halide lamp for 60 min. The reacted solution was centrifuged and the clear solution is used for photoluminescence measurements in a fluorescence spectro fluorometer (Fluoromax 4) with the excitation wavelength of 315 nm.

RESULTS AND DISCUSSION

XRD pattern of ground mixture consisting of stoichiometric amounts of BiOCl and Na₂WO₄ heat treated at 600 °C for 4 hrs and washed after cooling is shown in Fig. 1. All the observed diffraction peaks could be indexed to Bi₂WO₆ of JCPDS file No: 39-0256. Since there are no extra peaks, that could not be indexed, the sample is ascertained to be phase pure Bi₂WO₆.

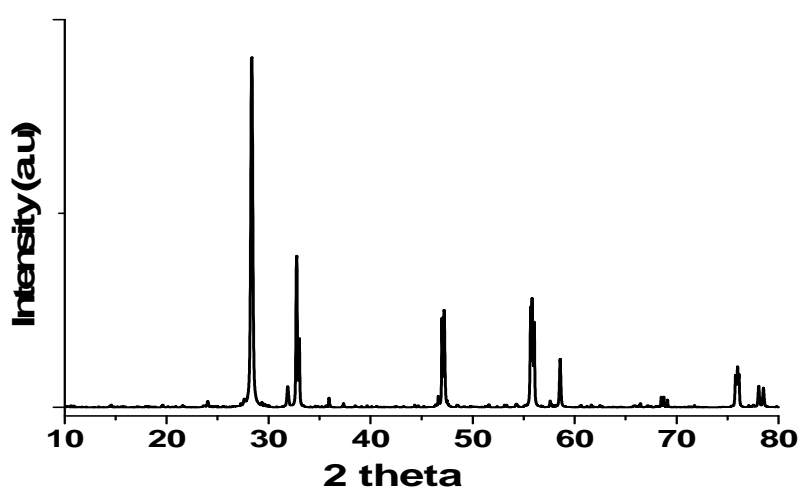


Fig. 1. XRD pattern of ground mixture of BiOCl+Na₂WO₄ heat treated at (a) 500°C and (b) 600°C for 4 hrs and washed with water

Temporal Variation of spectral contours for aqueous solutions of Brilliant Green (BG), BG + H₂O₂, BG + Bi₂WO₆ and BG + H₂O₂ + Bi₂WO₆ as a function of irradiation time are shown in Fig 2. BG shows a characteristic absorption at $\lambda = 610 \text{ nm}$ with very little photolysis caused due to irradiation for 240 min (Fig. 2a). In presence of H₂O₂, BG

undergoes photo degradation to an extent of 85% for 240 min of irradiation (Fig. 2b). In presence of Bi_2WO_6 photo degradation of BG to an extent of 65% is observed for irradiation 240 min (Fig. 2c). However, in presence of H_2O_2 + Bi_2WO_6 , complete 100% photocatalytic degradation of BG is achieved for 240 min of irradiation as can be seen from Fig. 2d.

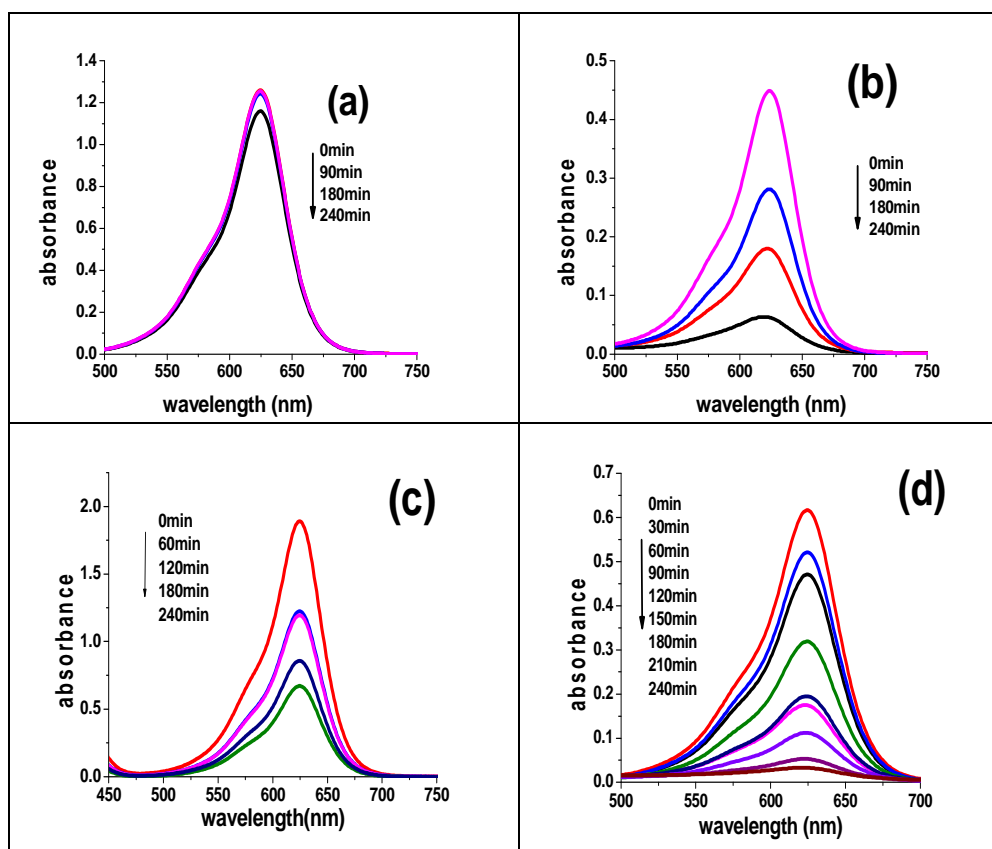


Fig. 2. Variation of spectral intensities as a function of irradiation time for (a) BG, (b) BG+ H_2O_2 , (c) BG+ Bi_2WO_6 and (d) BG + Bi_2WO_6 + H_2O_2

Variation of spectral intensities as a function of irradiation time for aqueous solutions of Carmine Indigo (CI), CI+ H_2O_2 , CI+ Bi_2WO_6 and CI+ H_2O_2 + Bi_2WO_6 are shown in Fig 3. From the figure, it is evident that CI has a characteristic absorption at $\lambda=610$ nm, and does not undergo any photolysis for irradiation up to 200 minutes (Fig 3a). In presence of H_2O_2 CI shows continuous photo degradation with progressive irradiation. For 200 minutes of irradiation, photo degradation to an extent of 88% is noticeable (Fig 3b). In presence Bi_2WO_6 , nearly 80% of photo degradation of CI is observed as seen from Fig 3c. However, in presence of both Bi_2WO_6 and H_2O_2 , complete 100% photocatalytic degradation of CI has been observed for irradiation of 135 min indicating a synergetic between Bi_2WO_6 , and H_2O_2 , (Fig 3d).

Time dependent variations of spectral contours with progressive irradiation for aqueous solution of Toluidine Blue (TB), TB+ H_2O_2 , TB+ Bi_2WO_6 and TB+ H_2O_2 + Bi_2WO_6 are shown in Fig 4. From figure 4a, it can be seen that TB has a characteristic absorption at $\lambda=625$ nm and TB undergoes photolysis to an extent of 12% for irradiation of 90 min. In presence of H_2O_2 , TB undergoes photo degradation to an extent of nearly 50% for 90 min of irradiation (Fig 4b). In presence of Bi_2WO_6 , photo degradation of TB to an extent of ~7% is observed for irradiation of 90 min as seen in Fig 4c. However, in presence of both H_2O_2 + Bi_2WO_6 , complete 100% photocatalytic degradation of TB is achieved for 75 min of irradiation, (Fig 4d).

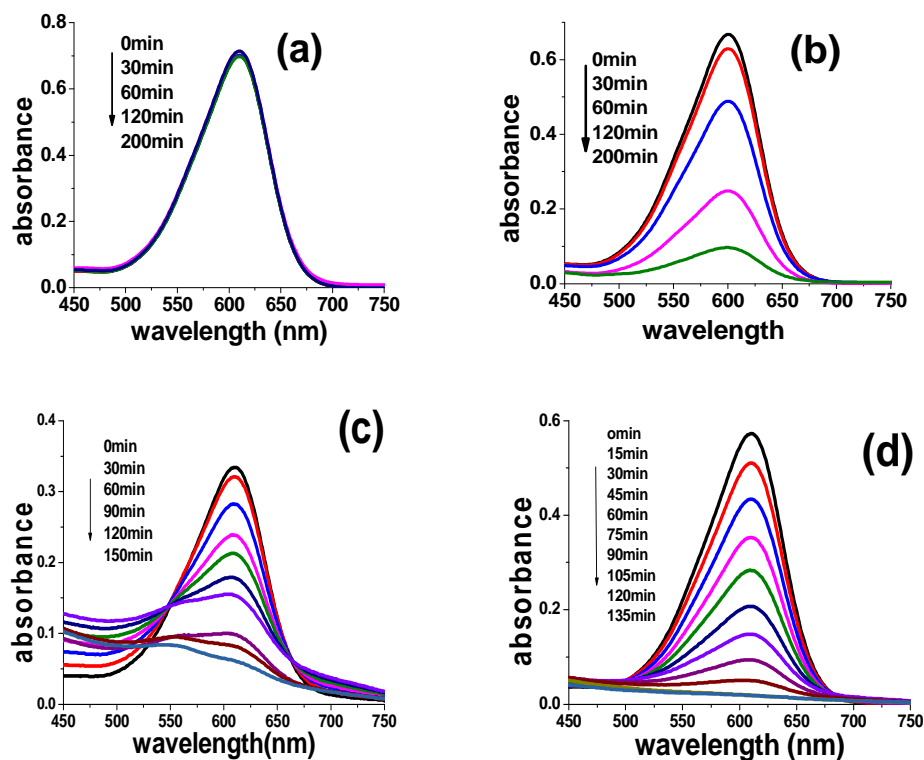


Fig. 3. Time dependent variation of spectral intensities as a function of irradiation time for (a) CI, (b) CI + H₂O₂, (c) CI + Bi₂WO₆ and (d) CI + Bi₂WO₆ + H₂O₂

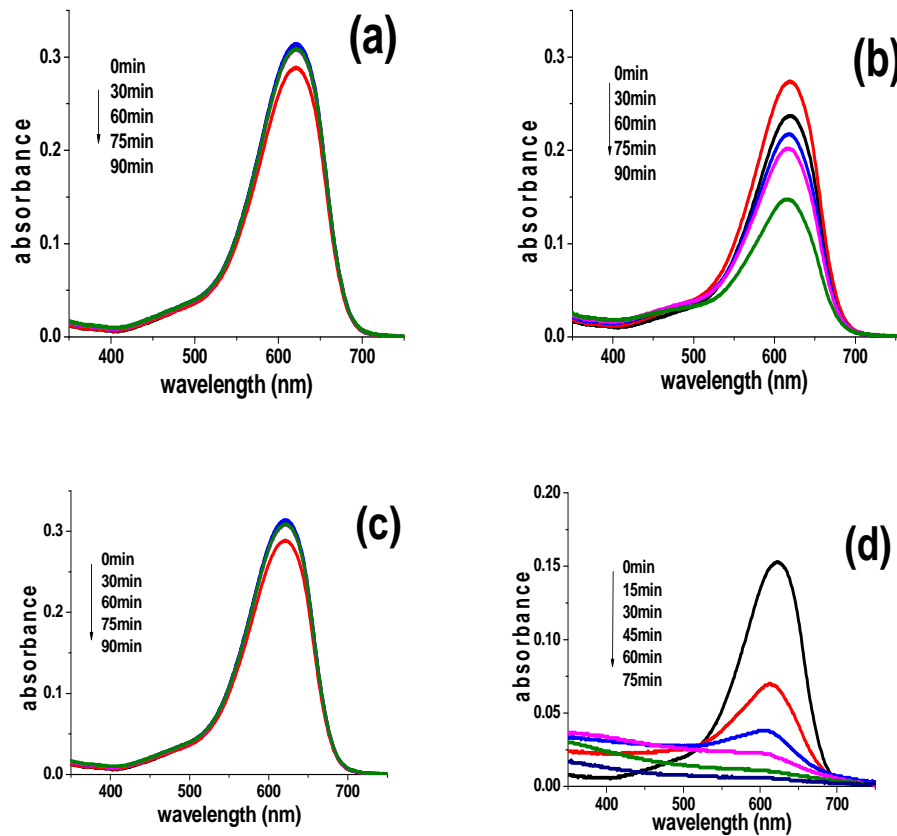
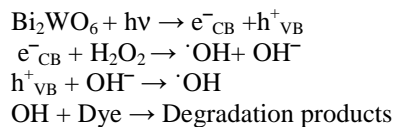


Fig. 4. Temporal variation of spectral contours as a function of irradiation time for (a) TB, (b) TB + H₂O₂, (c) TB + Bi₂WO₆ and (d) TB + Bi₂WO₆ + H₂O₂

Based on the experimental data obtained for the enhanced degradation of BG, CI and TB in presence of H₂O₂, photocatalytic degradation mechanism may be suggested as follows:



Formation of $\cdot\text{OH}$ during irradiation is ascertained by Photoluminescence studies using Terphthalic acid (TPA) as probe molecule. TPA reacts with $\cdot\text{OH}$ free radicals to form 2-hydroxy terphthalic acid (HTPA) which exhibits a characteristic luminescence peak at 420nm. Photoluminescence spectra for TPA+Bi₂WO₆ in water with and without H₂O₂ prior to and after irradiation are shown in Fig. 5. The intense peak observed after irradiation for Bi₂WO₆ + TPA + H₂O₂ is a clear indication of formation of $\cdot\text{OH}$ free radicals.

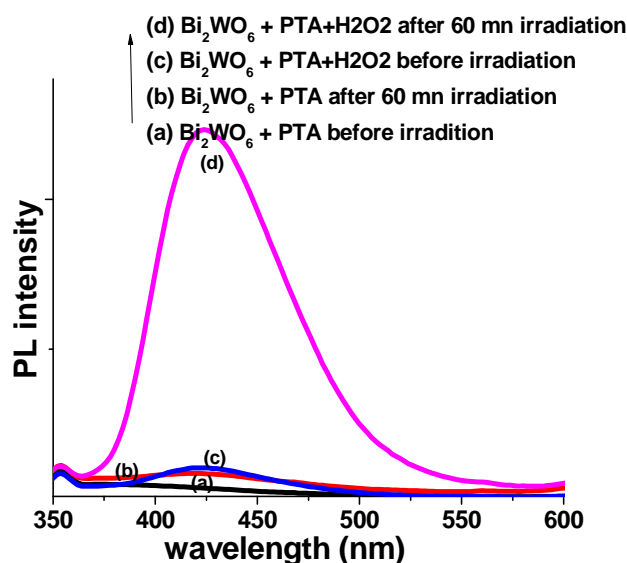


Fig. 5. Photoluminescence spectra of Bi₂WO₆+TPA with and without H₂O₂, prior to and after irradiation

Plot of $\ln(C_t/C_0)$ vs irradiation time for different reactions of dye, dye+H₂O₂, dye+Bi₂WO₆ and dye+Bi₂WO₆+H₂O₂ plotted for BG, CI and TB are shown in Fig. 6. Rate constants computed from the respective slopes for each are given in Table 1.

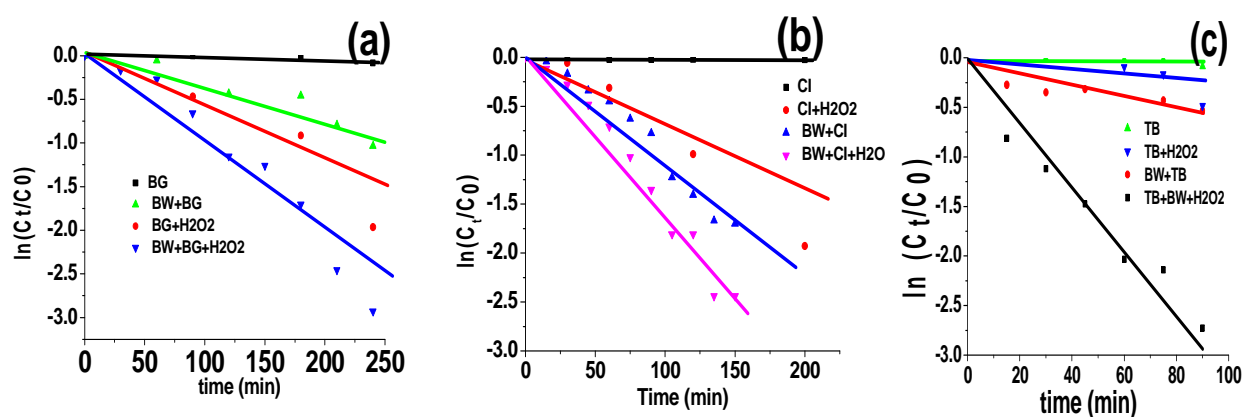


Fig. 6. Plots of $\ln C_t/C_0$ vs irradiation time for dye, dye+H₂O₂, dye+Bi₂WO₆ and dye+ Bi₂WO₆+H₂O₂ (a) BG, (b) CI and (c) TB

Table 1. Calculated rate constants for photo degradation of BG, CI and TB with and without catalyst and H₂O₂

Photo degradation	Rate constant k (min ⁻¹)		
	BG	CI	TB
Dye alone	0.0	0.0	1.1x10 ⁻⁴
Dye+H ₂ O ₂	2.5x10 ⁻⁵	5.3x10 ⁻⁵	7.2x10 ⁻⁴
Dye+Bi ₂ WO ₆	1.2x10 ⁻⁵	6.7x10 ⁻⁵	8.8x10 ⁻⁴
Dye+ Bi ₂ WO ₆ + H ₂ O ₂	4.2x10 ⁻⁵	1x10 ⁻⁴	4.2x10 ⁻³

CONCLUSION

Photocatalytic degradations of Brilliant green, Carmine indigo and Toluidine blue have been studied under visible light irradiation using visible light active Bi₂WO₆ prepared by solid state metathesis. Addition of H₂O₂ enhanced the rate of degradation in each case. Irradiation times of 240, 135 and 75 min are obtained for complete photocatalytic degradation of Brilliant green, Carmine indigo and Toluidine blue respectively. Formation of OH free radicals during irradiation in presence of H₂O₂ is ascertained by photoluminescence studies using terphthalic acid as probe molecule.

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