Influence of synthesis methods on physical and photocatalytic properties of Bi$_2$WO$_6$ for decomposition of organic dyes and Cr(VI) reduction

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Abstract. This article reports preparation of Bi$_2$WO$_6$ using solid-state and solution combustion methods. Different physicochemical characterization techniques such as XRD, SEM, TEM, BET-N 2 adsorption study, UV–vis, XPS and photoluminescence spectroscopy were used to examine crystalline phase, optical and morphological properties of synthesized Bi$_2$WO$_6$ samples. The evaluation of prepared photocatalyst for methyl orange degradation, Cr(VI) reduction under visible light and rhodamine B degradation under direct sunlight was carried out. The sample prepared by a solution combustion route, exhibited superior photocatalytic activities than that prepared by a traditional solid-state route.

Keywords. Mixed metal oxides; photocatalyst; methyl orange; rhodamine B; Cr(VI).

1. Introduction

Waste water from paper, textile, dying and some other industries include residual dyes, which are non-biodegradable. The hazardous substances from waste water are harmful to living organisms. The presence of harmful contaminants in water makes it unsuitable for its use. Taking into account the problems associated with polluted water, it is necessary to minimize water pollution by using different strategies. Heterogeneous photocatalysis has been proved to be a potential technique for the effective removal of the pollutants from aqueous and gaseous media [1]. Photocatalysis is an advanced oxidation process, produces strong oxidative environment by formation of strong oxidants which degrades maximum organic pollutants. This process has potential applications in the field of environmental remediation [2–4]. Semiconductor-based photocatalysis has attracted an attention of researchers for wastewater treatment and hydrogen generation by water splitting [5,6].

The different metal oxides and sulphides like ZnO, WO$_3$, TiO$_2$, ZnS and CdS were extensively used as photocatalyst in last decades. Because of structural stability, higher photocatalytic activity, abundance and non-toxicity, TiO$_2$ (anatase, $E_g = 3.2$ eV) was widely used. However, due to wide bandgap, TiO$_2$ is UV-active photocatalyst, hence limiting its applications [7]. Due to wide bandgap, the development of novel photocatalysts with narrow bandgap for pollution abatement has become an interesting topic of research.

Various semiconducting perovskite metal oxides (e.g., CaIn$_2$O$_4$, Bi$_4$Ti$_3$O$_{12}$, Bi$_2$MoO$_6$, NaTaO$_3$, Bi$_2$WO$_6$, SrTiO$_3$) have been studied for photocatalytic applications, both for degradation of organic pollutants and hydrogen generation (fuel) from water [8–12]. Perovskites having layered structure are found to be effective photocatalysts and more explored due to their high activity and stability [13,14]. Perovskites having layered structure comprised of interlayer spaces hence have more surface area for reaction than the perovskite-based materials without layered structure. Higher surface is available in layered perovskites and impart enhanced photocatalytic properties to them as compared to perovskites without layered structure [15].

Among the different metal oxides used as photocatalysts, Bi$_2$WO$_6$ having layered perovskite structure is widely studied in the literature. The photocatalytic property of Bi$_2$WO$_6$ prepared by solid-state route was first time demonstrated by Kudo and Hijii [16]. Bi$_2$WO$_6$ is an n-type semiconductor with bandgap energy (2.7 eV) lying in the visible region [17]. The layered structure of Bi$_2$WO$_6$ is favourable for effective transfer of photo-charges, thereby retarding their recombination [18].

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The valence band of Bi$_2$WO$_6$ is comprised of Bi 6p and O 2p energy levels, with minor involvement of Bi 6s hybrid orbitals. The large contribution to the bottom of conduction band of Bi$_2$WO$_6$ is by the W 5d energy levels; whereas Bi 6p contributes with smaller extent to this. The largely dispersed valence band of Bi$_2$WO$_6$ favourably mobilizes the photocharges and promotes the oxidative reactions [19–23]. Other bismuth-based oxides can also exhibit the photocatalytic activity when particles are of large size. The Bi$_2$WO$_6$ photocatalyst with larger particle size is prone to the fast recombination rate and comparatively low light absorption [27,28]. For enhancement of photocatalytic reaction, it is required to have delayed recombination of photo-generated charge carriers. The adsorption behaviour of impurities or pollutant molecules on the surface of photocatalyst and effective separation of photo-charges plays a vital role in photocatalytic activity. Increased surface area leads to the enhanced adsorption properties of the catalysts [29].

In fact, photocatalytic activity of photocatalyst is influenced by various characteristics, for example, crystalline phase, crystallite size, specific surface area and particle morphology. The chemical degradation of a pollutant occurs at the surface of the photocatalyst and consequently the surface properties of the catalyst have key role to play. Doping, loading metal, coupling with co-catalysts have been attempted to improve the photocatalytic properties. Synthesis methods also play crucial role and contribute significantly to improve the photocatalytic properties of the catalyst by changing the morphology and other related properties.

Different methods of preparation are reported for bismuth tungstate such as solid-state reaction, hydrothermal synthesis, amorphous complex precursor route, microwave-assisted solvothermal, combustion and sol–gel method [30–34]. In this article, we report for the first time the synthesis of Bi$_2$WO$_6$, which is designated as BW-2.

2.2 Characterization

X-ray powder diffraction (XRD) patterns of BW-1 and BW-2 samples have been collected on Rigaku Ultima IV diffractometer (Cu Kα) within 2θ range 10–80°. The BET surface area was determined by the N$_2$ adsorption at 77 K using a Micrometrics ASAP 2020. JEOL-JSM-5200 Scanning Electron Microscope (SEM) was used to record SEM images to observe morphology of BW-1 and BW-2 particles. Transmission electron microscope (TEM) images of particles were recorded on JEOL-JEM 2100 instrument operated at 200 kV. X-ray photoelectron spectrum (XPS) was recorded to identify the chemical states of constituting elements and surface composition of the sample. The diffuse reflectance (DRS) UV–visible spectra of BW-1 and BW-2 were recorded on a Shimadzu UV-2700 spectrophotometer (BaSO$_4$ was a reference). AvaSpec2048 spectrophotometer having LED excitation source (Oceans optics, LLS-345) with a wavelength of 345 nm was used for photoluminescence (PL) measurements.

2.3 Photocatalysis

The photoreactor made up of borosilicate glass (UV filter) was used for the photocatalytic experiments. In a typical experiment, 0.2 g (1 mg ml$^{-1}$) of catalyst was added in a MO solution (200 ml) having 5 × 10$^{-5}$ M concentration. The equilibrium was set up for dye molecules adsorption on the catalyst’s surface by stirring the solution for 30 min in dark. The photodegradation was started by irradiating the solution by visible light (400W metal halide Philips lamp) with constant stirring. During photocatalytic experiment, 5 ml dye solution was taken out of the reactor with interval of 30 min. Aliquots were centrifuged and the change in
concentration of irradiated MO solution was evaluated using Shimadzu model UV-2700 spectrophotometer. Similarly, the photocatalytic decomposition of Rh-B was attempted using direct sunlight by dispersing 0.1 g catalysts in $1 \times 10^{-3}$ M solution of Rh-B (100 ml).

Reduction of Cr(VI) was attempted under visible-light irradiation with constantly stirring the solution. In a typical experiment, 0.2 g catalyst was dispersed in Cr(VI) solution (200 ml, 20 ppm) and pH of the solution was maintained at 3. After 30 min time interval, 2.5 ml of the sample was taken out and mixed with 2.5 ml solution of 1,5-diphenylcarbazide (0.25%) solution, which developed a particular colour. The change in concentration of Cr(VI) depended upon change in intensity of colour developed, which was monitored with a spectrophotometer at $\lambda = 319$ nm (UV-2700, Shimadzu, Japan).

3. Results and discussions

The powder XRD patterns of the Bi$_2$WO$_6$ samples BW-1 and BW-2 are displayed in figure 1. The phase identification was carried out by including the simulated XRD data along with experimental XRD data of Bi$_2$WO$_6$. For simulation of XRD data of Bi$_2$WO$_6$, the structural details were used from crystallographic open database (COD 1567271) and the software package used was Mercury 3.2. The diffractograms of BW-1 and BW-2 are identical with the simulated pattern of Bi$_2$WO$_6$. The absence of any additional peak in XRD pattern due to precursors confirms the formation of Bi$_2$WO$_6$ in the pure form. Broadened XRD peaks in the pattern of sample prepared by solution combustion method (BW-2) is a characteristic of nanoparticle formation (100 nm x 30 nm by TEM analysis).

Morphology of the samples prepared in this study was examined by the SEM images. Bi$_2$WO$_6$ prepared by solid-state route (BW-1) shows the flakes morphology, which is characteristic of layered material (figure 2a). The BW-2 prepared via solution combustion method shows aggregation of smaller particles. Figure 2c depicts the TEM image of BW-1 sample, which indicate the formation of elongated particles (~700 nm x 305 nm). The BW-2 TEM images (figure 2d) confirm the crystalline aggregates of the particles with rod-like morphology having length ranging from ~100 nm to 300 nm and 30 nm width.

Diffuse reflectance UV–visible spectra of BW-1 and BW-2 samples are displayed in figure 3a. The absorption edge of BW-2 was found at 425 nm, which is almost similar to BW-1. Wood and Tauc method was used to determine bandgap energies ($E_g$) of the samples [35]. From the absorbance and photon energy, the bandgap value was determined using following equation:

$$\alpha \propto (h\nu - E_g)^n$$

where $h$ is a Planck’s constant, $\alpha$ is absorption coefficient, $\nu$ is photon frequency, $A$ the constant and $E_g$ the bandgap energy. The value of $n$ decides the particular type of transition in semiconducting material. The values of $n = 1/2$ indicate the allowed direct transition, while if $n = 2$ it is allowed indirect transition. When $n$ takes value of $3/2$ corresponds the transition is forbidden direct and it is forbidden indirect for $n = 3$. UV–Vis DRS plot indicated that there is allowed direct transitions in prepared sample since the value of $n$ is 1/2.

The $E_g$ value of BW-1 was calculated to be 2.352 eV and that of BW-2 was 2.437 eV (figure 3b). These $E_g$ values are appropriate to use BW-1 and BW-2 for photodegradation of dyes by visible-light illumination. The visible light absorption of BW-2 has significantly increased as compared to BW-1. Marginal increase in bandgap energy of BW-2 as compared to BW-1 was evidenced from the results of UV–vis data. The observed increase in bandgap energy depends on many parameters such as particle shape and size, grain size, structural phase as reported in literature [36–38]. Narrow bandgap energies of both the samples make easy excitation of electrons, which ultimately leads to the formation of abundant charge carriers when irradiated by visible light.

In general, surface area of photocatalyst used and rate of recombination of photo-charges produced are responsible for efficiency of photocatalytic reactions. For photocatalytic degradation reactions, large surface area enhances the catalytic activity due to increased adsorption of reactants over the surface of catalyst. The specific surface area of BW-1 and BW-2 was measured by BET method using the $P/P_0$ data in the range 0.05 to 0.35 (supplementary figure S1). The BET surface area of BW-2 was 1.5 m$^2$ g$^{-1}$ and was higher than that of BW-1 (BET = 0.005 m$^2$ g$^{-1}$). The increase in surface area of BW-2 sample enhances the contact area between the photocatalyst and the organic molecules; it is advantageous for photocatalytic activity enhancement of BW-2 [39].
The PL spectra of BW-1 and BW-2 samples with excitation wavelength 315 nm are displayed in figure 4. Both samples show strong emission peaks at 468 nm. The PL intensity of BW-2 was observed significantly lower than that of BW-1. Generally, for high quantum efficiency of photo-degradation activity of photocatalyst, it is essential to have stronger photo-generated charge separation. Lower the PL intensity stronger will be the photogenerated charge.
separation. PL results showed that BW-2 has lower PL intensity, stronger charge separation than BW-1. Thus, PL spectra indicated that the delayed recombination of the photo-charges was observed over BW-2, thereby enhancing its photocatalytic activity.

Figure 5a shows typical survey XPS spectrum of BW-2, which indicated the presence of Bi, W and O elements. Peak for C 1s was observed at binding energy of 285 eV, which was further used to correct binding energy values found from the XPS spectrum. From XPS (figure 5b), binding energies of W4f7/2 and W4f5/2 were found to be 35.198 and 37.349 eV, respectively, confirming +6 oxidation state of W [40,41]. Well intense peaks centred at 158.93 and 164.27 eV in XPS spectrum of Bi4f (figure 5c) were attributed to Bi4f7/2 and Bi4f5/2. The positions of these two peaks were having 5.34 eV difference of binding energies, typically found for Bi3+, confirming its presence in Bi2WO6 [42,43]. O1s XPS spectrum of oxygen (figure 5d) exhibited three strong peaks at binding energies of 530.14, 530.86 and 532.32 eV correspondingly been assigned to the lattice oxygen, surface –OH groups and absorbed water [44,45].

Photocatalytic activities of BW-1 and BW-2 samples were tested for MO degradation under visible light. The change in concentration of MO was monitored with regular time intervals (30 min). UV–visible absorption profile of MO dye solution with respect to time over BW-2 is displayed in figure 6a. It is evident from figure 6a that the significant amount of MO dye was degraded over BW-2 after 240 min. The comparative plot of degradation of MO (5 × 10⁻⁵ M) solution by BW-1, BW-2 samples and without catalyst is displayed in figure 6b. From this figure, it is evident that after 240 min, 74% MO was degraded over BW-2, which is considerably higher than 20% degradation of MO observed over BW-1. The rate of photo-degradation of MO over BW-2 is significantly higher than that over BW-1 (figure 6c). This increased extent of photo-degradation of MO by BW-2 sample is attributable to the smaller particle size of BW-2 and delayed recombination of electron–hole pair. The BW-2 retains its photocatalytic activity after three cycles, thus indicating the reusability of it (figure 6d).

The sample BW-2 was prepared at comparatively low temperature, having higher surface area but low degree of crystallinity. The sample prepared by solution combustion synthesis has high defects in its structure, which affect the rapid transfer of the photo-generated charges at the site of action. When such sample is irradiated by light, then these defects are responsible for recombination of electrons and holes, thereby retarding the photocatalytic activities. In such case, the smaller particle size of the sample makes avail a reduced pathway for photo-charges to reach to the surface of the photocatalysts from their site of generation. In the present case, the reduced pathway is dominant over the defects formed in the structure. Therefore, the sample prepared by solution combustion synthesis with lower particle size having higher surface area, have high photocatalytic activity than sample prepared by traditional solid-state synthesis.

To study the effect of amount of BW-2 on photodegradation rate, the experiments with different amount of photocatalysts were carried out (100 to 250 mg; difference 50 mg) for MO (5 × 10⁻⁵ M). The other reaction conditions such as pH, initial concentration of MO, reaction time were kept fixed. Supplementary figure S2 shows comparative plot of photodegradation of MO using different amounts of photocatalyst. The photocatalytic activity was increased from 32% for 100 mg to 80% for 250 mg after 240 min of visible-light irradiation. The increased amount of catalyst makes available the increased area for adsorption of dye, which is responsible for enhanced photodegradation of MO. To study the effect of initial concentration of MO on photocatalytic activity of BW-2, the reactions were carried out by changing the initial concentration of MO as 1 × 10⁻⁵ M, 5 × 10⁻⁵ M, 10 × 10⁻⁵ M. While doing so, other reaction conditions such as pH, amount of photocatalyst, irradiation time were kept constant. It was observed that under visible-light irradiation, almost all 1 × 10⁻⁵ M of MO degrades after 150 min. The photodegradation of 5 × 10⁻⁵ M MO dye solution in 240 min was 74%, which was 70% in case of 10 × 10⁻⁵ M of MO dye solution (supplementary figure S3). Increased concentration of MO results in adsorption of dye on photocatalyst surface, which retards photocatalytic degradation.

pH also plays a key role in photocatalytic degradation reactions. The effect of pH values on the photocatalytic decomposition of MO was evaluated by adjusting the pH of dye solution (5 × 10⁻⁵ M) in the range of 2–10, while the other experimental conditions were kept constant. The rate of degradation of MO was found to be decreased with increase in pH values (supplementary figure S4). The rate of photocatalytic degradation of MO was highest in acidic medium (pH = 2). This might be due to an availability of hydrogen ions, which absorb hydroxyl radicals formed, thereby retarding recombination of electron and holes.

Figure 4. Photoluminescence emission spectra of Bi2WO6 synthesized by solid–state synthesis (BW-1) and solution combustion synthesis (BW-2).
Therefore, pH = 2 was found to be an optimum condition for photocatalytic degradation of MO using BW-2.

The photocatalytic efficiency of BW-1 and BW-2 was further evaluated for Rh-B degradation under sunlight and visible light. The solar light intensity used was 760 μm^2 measured on TES solar power metre. In these experiments, 200 mg of photocatalyst was dispersed in 200 ml of 1 × 10^{-5} M Rh-B dye solution taken in 250 ml borosilicate beaker. It was observed that photocatalytic degradation of Rh-B under sunlight by BW-1 catalyst was 18% in 240 min, whereas it was 97% in 120 min for BW-2 catalyst (supplementary figure S5). From these results, it was revealed that BW-2 showed excellent photocatalytic activity for decomposition of Rh-B under sunlight than BW-1. Similarly, photocatalytic degradation of Rh-B dye was also carried out under visible-light illumination, which showed 100% degradation in 120 min. Photocatalytic degradation of Rh-B (1 × 10^{-5} M) by BW-2 in sunlight is shown in supplementary figure S5a, whereas supplementary figure S5b displays photocatalytic activity of BW-2 under visible light as well as sunlight. It was revealed that BW-2 degraded Rh-B in visible light and sunlight exactly to the same extent for same period of irradiation.

Photocatalytic efficiency of BW-1 and BW-2 was further evaluated for Cr(VI) reduction under visible light. Cr(VI) is lethal water pollutant; hence demands its removal from contaminated water or its reduction to Cr(III), a comparatively harmless form. The reduction of Cr(VI) was monitored by diphenyl carbazide method (λ_{max} = 540 nm). Figure 7a exhibited the change in concentration of Cr(VI) after particular time intervals. The results reveal that BW-2 reduces almost all of Cr(VI) to Cr(III) in 180 min of visible light irradiation. The rate of reduction of Cr(VI) over BW-2 was significantly high as compared to that using BW-1 as catalyst (figure 7b). After 150 min, only 20% of Cr(VI) was reduced over BW-1, and that was very low than that of the BW-2. The variation of concentration as a function of time is highly irregular in the case of MO degradation (figure 6a and b) and in first instance it might be due to the fact that, the MO is impure (purity 85%) dye and the impurities may behave differently or compete with dye during degradation. On the other hand, the variation of concentration with time in case of Rh-B and Cr reduction is linear (supplementary figure S5 and figure 7).

Degradation rate constant is a fundamental property of a photocatalyst and hence it can be conveniently used to
compare the performance of various photocatalysts for the same reaction. Such comparison data reported for dye degradation under visible light or sunlight is included in table 1. In the present study, the rate constants for dye degradation reaction and Cr reduction reaction were determined by assuming pseudo first-order model ($k_{app} = \ln(C_0/C_t)$, where $C_0$ is initial concentration and $C_t$ is concentration after time $t$). BW-2 sample demonstrated
the superior performance as compared to Bi$_2$WO$_6$ photocatalysts prepared by various methods. The rate constant for RhB degradation over Bi$_2$WO$_6$ prepared by hydrothermal method reported in literature [46] is $8.9 \times 10^{-3}$ min$^{-1}$. Other Bi$_2$WO$_6$ photocatalysts prepared by hydrothermal method show very low rate constants for RhB photodegradation, e.g., $1 \times 10^{-3}$ min$^{-1}$ [47] and $2.8 \times 10^{-3}$ min$^{-1}$ [48]. The rate constant for RhB photodegradation over BW-2 prepared in this study by solution combustion method is $12 \times 10^{-3}$ min$^{-1}$. Also the Bi$_2$WO$_6$ prepared by solid-state method [49] is found to have rate constant of $3 \times 10^{-3}$ min$^{-1}$ for Cr reduction, while that for BW-2 prepared by solution combustion method is $4 \times 10^{-3}$ min$^{-1}$. 

### 4. Conclusion

The Bi$_2$WO$_6$ photocatalysts with a narrow bandgap were successfully synthesized by solid-state and solution combustion methods. The results showed that the method of synthesis had a significant influence on photocatalytic performance of the photocatalysts. The highest degradation efficiency was observed for BW-2, which can degrade 74% MO in 240 min and Rh-B completely in 120 min. BW-2 has compatible photocatalytic performance for degradation of RhB under sunlight as well as visible light. Furthermore, the complete reduction of Cr(VI) in 180 min under visible-light irradiation demonstrated the excellent photocatalytic performance of BW-2. These versatile and highest photocatalytic properties were ascribed to the smaller particle size, enhanced surface area and increased adsorption capacity of BW-2. The highest degradation of MO observed over BW-2 in acidic medium is advantageous as most of the industrial wastewater has acidic pH. BW-2 has also decomposed Rh-B with the concentration of $10^{-5}$ mol l$^{-1}$, making it suitable for treatment of wastewater with a higher load of Rh-B. The excellent activity of BW-2 for the reduction of Cr(VI) into Cr(III) is promising to consider the preparation of photocatalyst by low temperature methods to have enhanced photocatalytic activities. The solution combustion method is a simple, rapid, low-cost method for preparation of efficient Bi$_2$WO$_6$ with enhanced activities.

### References

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<table>
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<th>Degradation (%)</th>
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<td>[49]</td>
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Table 1. Degradation/photoreduction rate constants (from literature) for Bi$_2$WO$_6$ synthesized by various methods.
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