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Abstract: A novel visible– light driven photocatalyst, BIMNVOX.x was synthesized by ethylene glycol–citrate sol–gel route and microwave- assisted calcination. The photocatalyst was characterized structurally by X–ray powder diffraction (XRPD) and simultaneous thermogravimetric–differential thermal analysis (TG–DTA). Its optical and surface properties were determined by means of UV–vis absorption spectrophotometry and BET– nitrogen adsorption isotherm measurements, respectively. The photocatalytic efficiency of BIMNVOX.x system was investigated by applying the pseudo first- order kinetic model to the photocatalytic degradation reaction of crystal violet, CV dye in aqueous solution under visible light irradiation. The β (orthorhombic) –BIMNVOX phase, space group Acam exhibited the highest photocatalytic degradability, indicating that the photocatalytic efficiency of BIMNVOX catalyst is essentially enhanced by the increased number of catalyst active sites, irrespective of the kind of phase stabilized and the increasing photoabsorption ability with Mn dopant content. Moreover, the possible photocatalytic degradation mechanism of aqueous CV dye solution under visible light irradiation was also proposed.

Keywords: Photocatalyst, BIMNVOX, Microwave- Assisted Calcination, Crystal Violet, Perovskites

1. Introduction

Dye pollutants released with industrial wastewater are an important source of environmental concern. Organic dyes are widely used in industrial processes and domestic activities, leading to esthetic pollution, eutrophication, and perturbations in aquatic life [1,2]. Crystal violet (CV) is a member the triphenylmethane family of dyes that has several industrial and biological applications. This large family is used extensively in a variety of industrial process, but many are also known to have carcinogenic and mutagenic properties[3,4]. Advanced oxidation processes (AOPs) have been proposed and widely investigated for the photodegradation of organic dyes in industrial wastewaters. Semiconductor mediated photocatalysis has been found to be potentially advantageous, as it costs less money and does not create secondary contamination [5]. Among known semiconductor photocatalysts, TiO2 has been extensively studied for photocatalytic and photochemical applications because of its thermal stability, facile synthesis, low cost and the low toxicity (Zhang et al. 2006). However, because of its relatively high band–gap, TiO2 (3.2 eV) is activated only by ultraviolet light with wavelengths shorter than 387 nm [6,7], which severely limits its commercial application for water and wastewater treatment. Hence, many researches have been devoted to find, design and optimize efficient semiconductor photocatalysts with maximum absorption thresholds (minimum band gaps) that effectively accelerate the photocatalytic degradation of organic dyes, when irradiated in the visible light region.

Very recently, a layered perovskite– type Bi4V2O11 oxide and its metal– doped analogues, designated as BIMEVOX.x (Bi2Me4V1−xO5.5−(5−x)/2− x2; l=Me oxidation state) belonging to the Aurivillius family, have attracted considerable attention
due to their interesting propriety, such as in peculiar polymorphic structure and stability [8,9,10], very low electrical conductivity below 300 °C [11], reasonable scale–

electronic and ferroelectric contribution at low dopant

concentrations [12,13], and remarkably narrow band gap with a

potential visible light photocatalytic efficiency [14,15].

BIMEVOX materials, such as BIALVOX, BIGAVOX [14]

and BINIVOX [16] have shown enhanced photocatalytic
degradation of some organic dyes in the visible spectral range as

the consequence of band gap narrowing of the doped
photocatalysts.

In the present paper, we report a novel visible–light driven
photocatalyst, BIMNVOX.x Bi5Mn1+Vx/3+V1-xO5.5-x/2 for the
photodegradation of organic dyes in industrial wastewaters. A
series of BIMNVOX.x was synthesized by ethylene

glycol–citrate sol–gel route and the resulting V and Mn
containing xerogels were calcined by the microwave heating

using a modified domestic microwave oven. The

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glycol–citrate sol–gel route and the resulting V and Mn
containing xerogels were calcined by the microwave heating

using a modified domestic microwave oven. The
photocatalytic properties of the BIMNVOX.x catalyst were
then investigated on the photodegradation of CV dye under
visible light irradiation.

2. Experimental

2.1. Catalyst Preparation

Analytical grade Bi(NO3)3.5H2O, NH2VO3 and
Mn(NO3)2.4 H2O were used as starting materials. Stock
solutions of the starting materials (0.1 M) were prepared by
dissolving an accurately weighed amount of corresponding
material in deionized water. A 0.2 M citric acid solution used

as chelating agent was prepared in deionized water–
ethylene glycol mixture at a volumetric ratio of 3:1. A 0.5 M NH3
solution was also used for adjusting pH.

The starting materials solutions were mixed at a volumetric
ratio of 2: x: (1–x) = Bi: Mn: V with citric acid solution to form
sol solutions. The ratio of citric solution to total metal ions
was set at 1.5:1. The pH of resulting sol solutions were
adjusted to ~7 by adding ammonia solution. The sol solutions
were then heated at 80°C under constant stirring for two hrs to
form visible gel. Wet gels were further dehydrated in an oven
at 90°C for 12 hrs to remove excess water and obtain dried
xerogels.

The xerogel was thoroughly mixed in an agate mortar for
further homogenization and then divided into two equal
portions. The first portion was thermally calcined in a muffle
furnace at 550°C for 6 hrs, while the second portion is
subjected to a microwave–assisted calcination for 25 min in a
modified microwave oven operated at a frequency of 2.45
GHz.

2.2. Structural Characterization of Photocatalyst

The stabilized phases and crystallite sizes for synthesized
samples of photocatalyst were determined by the X–ray
powder diffraction (XRPD) patterns obtained from a
Rigaku/Max–B X–ray diffractometer using Ni–filtered CuKα
radiation. The diffraction beams were collected using a 2θ2θ
geometry in the range of 15°≤ 2θ ≤ 80° with an increment of
0.05° at sctime of 0.8 sec/increment. The unit cell
parameters were refined using an X'Pert Plus software
program. The average crystallite size was calculated from the
diffraction line broadening via the Scherrer equation:

\[ D = \frac{0.9λ}{B \cos θ} \]  

where D is the crystal size in nm, λ is the CuKα radiation
wavelength (λ=1.54060Å), B is the half–width of the peak in
radians and θ is the corresponding diffraction angle.

The thermal decomposition of xerogel and the polymorphic
structure were investigated by thermogravimetric –
differential thermal analysis (TG–DTA) using a Perkin Elmer
thermal analyzer at a heating rate of 10 °C min⁻¹, running up

1000°C with an air flow rate of 30 ml min⁻¹. α–alumina was

used as a reference material. The microwave- assisted
decomposition of xerogel as a function of calcination time was
also followed by the X–ray powder diffraction.

2.3. Optical and Surface Properties of Photocatalyst

The optical band– gap energies (Eg) for the photocatalyst
series were estimated from UV–vis absorption spectra,
collected on a Shimadzu Scan UV–vis spectrophotometer
(UV–1240) at room temperature in the wavelength range
200–750 nm. The direct band– gap energy was calculated
from the wavelength corresponding to the band–gap edge
absorption (λedge) using equation (2) [17]:

\[ E_g (eV) = \frac{1240}{λ_{edge} (\text{nm})} \]  

Surface area measurements were performed by nitrogen
adsorption– desorption isotherm at 77 K on an Autosorb–1(Quantachrome) adsorption apparatus. The
adsorption data were collected in the nitrogen partial pressure
(P/Po) range of 0.01–0.99. The specific surface areas (SBET)
expressed in m²/g, were calculated by Brunauer–Emmett–Teller (BET) method.

2.4. Photocatalytic Activity Measurements

A 250–ml aqueous solution of CV dye (5 × 10⁻⁴ M) at pH
~10.0 (adjusted with diluted aqueous solution of NH3 and
H2SO4) was placed in a 450 ml – photoreactor equipped with a
magnetic stirrer. Before photocatalytic reaction, 200–mg
powdered sample of the photocatalyst was dispersed in the dye
aqueous solution. The resulting suspension was then
magnetically stirred in the dark for 25 min to reach the
adsorption–desorption equilibrium. The visible light with
wavelengths greater than 400 nm using a 300–W Xe lamp was
irradiated perpendicularly to the surface of solution at affixed
distance between the visible source and the surface of dye
solution (25 cm). At specific time intervals (10 min) about 5
ml– aliquot of the reaction mixture was withdrawn from the
photoreactor and then filtered to separate the catalyst residues.
The concentrations of dye versus irradiation time were
determined by measuring the maximum absorbance ($\lambda_{\text{max}}=590$ nm) using a Shimadzu UV–vis spectrophotometer (UV–1240). The photocatalytic activity of the BIMNVOX.x catalyst as a function of composition for the dye photodegradation was investigated using a pseudo first–order kinetic model.

$$\ln\left(\frac{C_t}{C_o}\right) = -k_{\text{app}} t$$

(3)

where $C_o$ and $C_t$ are the initial concentration and concentration at time, $t$ of CV dye solution, respectively and $k_{\text{app}}$ denotes the apparent first–order rate constant.

3. Results and Discussion

3.1. Structural and Polymorphic Properties of Photocatalyst

Figure 1 presents TG–DTA thermogram of BMNVOX.13 xerogel, which clearly shows a two–step thermal degradation, starting from 77 °C and extending upto 449 °C. Two thermal events are accompanied with the overall decomposition; a small endothermic and sharper exothermic peak which are observed at 192 °C and 449 °C, respectively. However, the first weight loss of the thermal degradation (~5.4 %), corresponding to the endothermic peak is attributed to elimination of physically adsorbed ammonia and water from the xerogel. It is also possible that free ammonium citrate and ethylene glycol are partially decomposed in this step. The second weight loss (~ 41.3 %), corresponding to the exothermic peak is associated with a fast decomposition and decarbonization of chelating citrate and ethylene glycol [13,18].

Figure 1. TG–DTA thermogram of as–prepared BMNVOX.13 xerogel.

The variation of XRPD patterns of the BIMNVOX.13 xerogel with time of microwave–assisted calcination at 2.45 GHz are presented in Figure 2. It can be observed that the xerogel is calcined and well- crystallized under microwave heating for 25 min as clearly evidenced by the existence of a characteristic singlet diffraction peak 110 around 2\(\theta\) ~ 32.5°. For compositions with $x = 0.10$, the singlet indexed 220, shows the existence of orthorhombic $\beta$–BIMNVOX phase of higher symmetry having space group Acam [19]. However for $x \geq 0.13$, the tetragonal $\gamma'$–BIMNVOX.13 phase, space group, I4/mmm is stabilized as clearly evidenced by the convergence of the sub–lattice doublet ca. 2\(\theta\) ~ 32.5° into a singlet indexed in tetragonal cell as (110) at 2\(\theta\) ~ 32° [20]. It is worthwhile to appoint that our structural characterization is found to be in a perfect agreement with what have been reported earlier for the BIMNVOX system [21].

Values of unit cell refinement, average crystallite size and crystallographic density obtained from fitting diffraction patterns are listed in Table 1. It is clear that the substitution of Mn into the Bi\(_4\)V\(_2\)O\(_{11}\) compound causes a dramatic increase in the unit cell dimensions, accompanied by the same trend in the overall cell volume. The density and particle size both are found to increase slightly with the increase of Mn dopant content. This trend is in a good agreement with the variation of unit cell parameters, and reflecting the positive contribution of Mn substitution to the overall lattice expansion as a result of the incorporation of Mn (IV) dopant ions of larger ionic radius (0.72 Å) into the perovskite vanadate layers in the place of pentavalent vanadium sites (0.54 Å) as revealed earlier [22].

DTA thermograms depicts thermal stability of the BIMNVOX.x system and onset temperature of phase transitions (Figure 4). The two characteristic endothermic peaks clearly seen for the parent compound, Bi\(_4\)V\(_2\)O\(_{11}\) (x=0) as

Figure 2. XRPD patterns of the BIMNVOX.13 xerogel calcined by microwave–assisted route at 2.45 GHz as a function of time.
well as the substituted photocatalyst with composition, \(x=0.05\) are attributed to the consequent \(\alpha\rightarrow\beta\) and \(\beta\rightarrow\gamma\) transitions [23-25]. In addition, the heat flow per unit mass of the \(\alpha\rightarrow\beta\) transition is found to be nearly three orders of magnitude higher than that of the \(\beta\rightarrow\gamma\) transition. However, the \(\beta\)–BIMNVOX.10 photocatalyst shows a single endothermic peak 469 °C, assigned to the \(\beta\rightarrow\gamma\) transition, while the occurrence of order → disorder, \(\gamma'\rightarrow\gamma\) transition is observed for the \(\gamma'\)–BIMNVOX.13 phase [25, 26].

Table 1. Refined unit cell parameters, crystallographic densities, average crystallite sizes and specific surface areas of as–prepared BIMNVOX.x photocatalyst series.

<table>
<thead>
<tr>
<th>(x)</th>
<th>Unit cell parameters</th>
<th>(d) (g cm(^{-3}))</th>
<th>Average crystallite size ((\mu)m)</th>
<th>BET surface area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.521</td>
<td>5.627</td>
<td>15.293</td>
<td>475.10</td>
</tr>
<tr>
<td>0.05</td>
<td>5.611</td>
<td>5.623</td>
<td>15.387</td>
<td>485.47</td>
</tr>
<tr>
<td>0.10</td>
<td>5.624</td>
<td>5.633</td>
<td>15.453</td>
<td>489.55</td>
</tr>
<tr>
<td>0.13</td>
<td>5.631</td>
<td>5.639</td>
<td>15.508</td>
<td>491.73</td>
</tr>
</tbody>
</table>

3.2. Optical and Surface Properties of Photocatalyst

UV–vis absorption spectra of BIMNVOX.x photocatalyst for various compositions are presented in Figure 5. The intrinsic band–gap absorption of Bi\(_4\)V\(_2\)O\(_{11}\) is clearly seen at ~559 nm, resulting from the electronic transitions from Bi\(_6s/O_2p\) orbitals of the bismuthate (Bi\(_2\)O\(_2\))\(^{2+}\) layers (valence band) to V\(_{3d}\) orbitals of the (VO\(_{3.5}\))\(^{2-}\) perovskite–like slabs (conduction band) [14, 15], where \(\square\) represents an oxygen vacancy in vanadate polyhydra. The absorption edges of the BIMNVOX.x photocatalysts are found to shift toward longer wavelengths as the concentration of Mn dopant increases. This is without a doubt attributed to the additional contribution of Mn\(_{3d}\) orbitals to the conduction band [16] and increasing oxygen vacancy concentration [24, 27] in the perovskite vanadate layers. The variation of the optical band–gap energy of the BIMNVOX.x catalyst with Mn dopant concentration is illustrated in Table 2. It can be noted that the absorption edge of the BIMNVOX system is shifted towards the visible light region with the increasing Mn content compared to the pure Bi\(_4\)V\(_2\)O\(_{11}\). However this narrowing of band–gap energies is also accompanied by an increase in the specific surface areas (\(S\)\(_{BET}\)), suggesting that the Mn–doping strategy might play a positive contribution to the photoabsorption and photocatalytic activities of doped photocatalyst. This behaviour may be explained by the fact that the increasing Mn substitution leads to creation of oxygen vacancies at the equatorial planes of perovskite vanadate layers [13, 28]. Such oxygen vacancies not only extend the
optical absorption edge into the visible light region, but also serve as active sites available for the dye molecules to adsorb on the surface of photocatalysts and due to which their photocatalytic degradation becomes effectively enhanced [29].

Table 2. Values of band–gap energy for the BIMNVOX.x photocatalyst

<table>
<thead>
<tr>
<th>x</th>
<th>E_g (eV)</th>
<th>SD</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>559.08</td>
<td>2.22</td>
<td>0.03544</td>
</tr>
<tr>
<td>0.05</td>
<td>597.91</td>
<td>2.07</td>
<td>0.02446</td>
</tr>
<tr>
<td>0.13</td>
<td>604.58</td>
<td>2.05</td>
<td>0.04114</td>
</tr>
</tbody>
</table>

3.3. Photocatalytic Efficiency and Proposed Mechanism

The UV–vis spectrum of CV dye solution before photolysis and photocatalytic degradation, shows a main absorbance in visible light region at 590 nm (Figure 6). The value of C_o and C_t were obtained from the corresponding absorbance, measured at this wavelength. The variation in the photocatalytic degradation efficiency of CV dye with pure Bi_4V_2O_11 and doped BIMNVOX.x samples at varying Mn concentration is presented in Figure 7. It can be observed that the photodegradation of CV dye proceeds more rapidly when catalyzed by the BIMNVOX.x system, whose Mn content lies in the compositional range of the β– phase stabilization. It is worthwhile to appoint that this result is contrary to what have been reported very earlier for the BINIVOX.x photocatalyst [16], where compositions with stabilized γ– phase have shown a maximal photocatalytic efficiency.

The values of $k_{app}$ (min^{-1}) were calculated from the slope using the line–regression fitting to the first–order kinetic model as shown in Figure 8. Table 3 illustrates the variation of $k_{app}$ with Mn dopant level incorporated in the photocatalyst along with the regression determination coefficients ($R^2$). The highest photocatalytic degradability exhibited by the BIMNVOX catalyst with stabilized β– phase ($k_{app} = 8.45 \times 10^{-3}$ min^{-1} for $x=0.10$) indicates that the photocatalytic efficiency of BIMNVOX catalyst is essentially enhanced by the increased number of catalyst active sites, irrespective of the kind of phase stabilized and the increasing photoabsorption ability with Mn dopant content. The important point to be emphasized here is that the number of photocatalyst active sites reaches its maximum at $x=0.10$, which is in a good agreement with the expected optimal concentration of oxygen vacancies created at the equatorial planes the perovskite vanadate layers. This can also be evidenced by the lowering in the photocatalytic activity beyond this value of Mn content ($k_{app} = 6.96 \times 10^{-3}$ min^{-1} for $x=0.13$).

However, the decreased photocatalytic efficiency of γ–BIMNVOX.x catalyst for $x=0.13$, despite its highest ability to absorb visible light($E_g=2.05$ eV), may be attributed to the creation of oxygen vacancies at apical positions of the perovskite vanadate layers [16,17]. These apical vacancies are not only considered as inactive sites on the photocatalyst surface, they may also play a role in the fast recombination of the electron–hole pairs, and thereby slowing down the photocatalytic degradation.
The photocatalytic mechanism of CV dye degradation using the BIMNVOX.x catalyst under visible light irradiation can be explained by the fact that the Mn doping initially narrows the band gap of the photocatalysts to enhance visible light absorption [17]. The CV dye molecules are then adsorbed onto the perovskite vanadate layers as a result of a coulombic interaction between negatively charged oxygen atoms of the vanadate layers and the dye molecules with positively conjugated chromophore. Under irradiated visible light energy, the mechanism suggests that excitation of the adsorbed CV dye takes place by visible light absorption to the appropriate singlet or triplet states, subsequently followed by electron ejection from the excited dye molecule onto the conduction band, while the dye is converted into a cationic dye radical (CV•+) that undergoes degradation to yield mineralization products. The dye photocatalytic degradation reactions can be schematically summarized in Figure 9 [16, 29-31]. The resulting radical (OH•), being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most dyes to the mineral end products.

**Figure 9.** Proposed mechanism of CV dye degradation by BIMNVOX.x photocatalyst under visible light irradiation.

## 4. Conclusions

A novel Aurivillius- type BIMNVOX.x photocatalyst was successfully synthesized by ethylene glycol–citrate sol–gel route and microwave- assisted calcination. It has been found that the increase of Mn (VI) dopant content (x) in the BIMNVOX.x photocatalyst result in narrowing of band- gap energies, accompanied by the increase in the specific surface areas (S BET), and thereby enhancing the photoabsorption and photocatalytic activities of doped photocatalyst. It is interesting to note that the highest photocatalytic degradability, exhibited by the β– stabilized BIMNVOX.x phase for x=0.10, indicates that the enhancement of photocatalytic efficiency of BIMNVOX catalyst is attributed to the optimal concentration of oxygen vacancies (catalyst active sites) created at the equatorial planes of the perovskite vanadate layers, irrespective of the kind of phase stabilized and the increasing photoabsorption ability with Mn dopant content.

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**References**


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