

Effective Visible Light Photo Degradation of Nitrobenzene using BiVO₄ Prepared by Room Temperature Solid-State Metathesis

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Abstract: Photochemical degradation of nitrobenzene is studied using monoclinic BiVO₄ under visible light irradiation. *m*-BiVO₄ is prepared by room temperature solid-state metathesis reaction between BiOCl and NaVO₃ and characterized in terms of XRD, and SEM. Photocatalytic studies indicated that complete degradation of nitrobenzene occurred for 120min of irradiation.

Keywords: Photocatalysis, Nitrobenzene, Bismuth Vanadate, Solid-State metathesis

1. Introduction

Nitrobenzene (NB) is widely used in the production of dyes, explosives and pesticides. Even at low concentrations, NB causes high risk to human as well as ecological health. Waste water containing more than 2mg NB/L has been declared as hazardous by the U.S. Environmental protection agency. Continuous exposure to NB can lead to liver as well as kidney damage in human beings [1]-[4]. NB is resistant to chemical and biological degradation because of the strong electron affinity of -NO₂ group. Though several methods like adsorption [5], photochemical reduction [6], ozonation [7], oxidation by O₃ under U.V. irradiation [8], photoassisted Fenton oxidation [9], supercritical oxidation [10] and reductive degradation by zero valent iron [11] have been proposed for the remediation of NB from aqueous media, these methods are not completely successful and cost effective. In the last two decades there has been a growing interest in the semiconductor mediated heterogeneous photocatalysis for the non-specific oxidation of toxic organic pollutants from industrial waste water effluents [12].

Praveen surolia and Raksh Jasra [13] reported 59% degradation of NB for 240min of U.V irradiation over Eenglehard titanosilicate M-ETS-4 (M=Fe, Co, Ni, Cu and Ag) and concluded that Ag⁺ ions showed pronounced enhancement in photocatalytic activity. Weiping Wang and coworkers [14] reported 75% degradation of NB in 240min using H₃PW₁₂O₄₀/TiO₂ under sun light. Thou-Jen wang et al [15] reported photocatalytic degradation of NB at pH=4 over TiO₂ for 180min of U.V irradiation and air bubbling. Edger Alonso et al [16] reported 97% photodegradation of NB over 0.5 atomic % of Zn in TiO₂ under U.V irradiation. Hanwa Sidi Aliyu and coworkers [17] reported removal of 70% NB in 120min under visible light by coupled grafted cassava/ZnO. Ino Nitoi et al [18] reported degradation of NB using heavy metal doped TiO₂ at pH=4 for 240min of U.V irradiation. Wan-Kuen Jo et al [19] reported enhanced photocatalytic degradation of aqueous NB over graphitic carbon-TiO₂ composites under U.V irradiation for 240min. Hanwa Sidi Aliyu and coworkers [20] reported the use of visible light for 87% photodegradation of NB in 120min using microwave synthesized coupled Cu/ZnO

nanocomposite. So far no studies have been reported on the use of BiVO₄ for photocatalytic degradation of NB even though BiVO₄ is reported to be an excellent visible light active catalyst with a highly useful band gap of 2.4 eV. The present work is therefore aimed at to investing photodegradation of NB under visible light irradiation over monoclinic BiVO₄ synthesized by a newly developed solid-state metathesis reaction at room temperature.

2. Experimental

2.1 Synthesis of photocatalyst

Stoichiometric amounts of BiOCl (Loba Chemie PVT. Ltd.) and NaVO₃ (98% HIMEDIA) in the molar ratio of 1:1 are mixed in an agate mortar for 2hrs in ethanol with progressive grinding the mixture exhibited a canary yellow colour. After 2hrs of grinding the mixture is washed several times with distilled water to completely remove the bye product NaCl and the residue is dried at 80°C in an air oven. The dried powder is subjected to phase identification, microstructural investigation and photocatalytic studies.

2.2 Characterization

Phase purity of the resultant powder obtained at Room temperature and Calcined powder was investigated with X-ray diffractometer (PANalytical- X^{''} Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K_α radiation (λ= 1.54059 Å), with a scan rate of 2° min⁻¹.

2.3 Photocatalytic studies

Photo catalytic activity of BiVO₄ was evaluated in terms of degradation of NB under visible light. 10 mg of the catalyst powder was added into 100ml NB aqueous solution (10 mg/L) and the suspension was magnetically stirred for half an hour in dark to ensure adsorption/desorption equilibrium between photo catalyst powder and dye. The suspension was then exposed to 400 wt metal halide lamp; 5ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. The spectra as a function of irradiation time were obtained

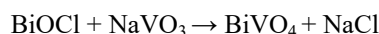
using UV-Visible spectrophotometer. The extent of photodegradation was calculated using the following reaction:

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

where A_0 and A_t correspond to the initial absorbance and absorbance at time t , respectively.

3. Results and Discussion

BiVO_4 is known to exist in three crystalline modifications namely tetragonal zircon, monoclinic scheelite and tetragonal scheelite. Even though all the three polymorphs contain vanadium in tetrahedral coordination, only monoclinic scheelite in which Bi-O polyhedra is more distorted is reported to exhibit visible light induced photocatalytic activity [21]. Synthesis of BiVO_4 has been reported in terms of solid-state [22], precipitation [23], solvothermal [24], sonochemical [25], hydrothermal [26], spray pyrolysis [27], and combustion [28] methods. In general, monoclinic BiVO_4 is obtained by high temperature processes [21], while tetragonal BiVO_4 results in aqueous lower temperature processes. Synthesis of *m*- BiVO_4 at room temperature has been reported from this laboratory in terms of solid-state metathesis between the reactants BiCl_3 and Na_3VO_4 [29]. However, since Na_3VO_4 is rather costly, a new approach is now pursued in the present study based on the following reaction.



Solid-state metathetic reactions are extremely fast, self-energetic and yield crystalline products. It allows the exchange of reaction partners where in the lattice energy of the co-product will be the driving force for the reaction. Grinding the reactants expedited metathetic reaction between the two reactant solids resulted in the formation of BiVO_4 . X-ray diffraction patterns of the ground mixture before and after washing to remove NaCl are shown in Fig.1. Prior to washing, the mixture showed diffraction peaks characteristic of a biphasic mixture consisting of BiVO_4 and NaCl. After washing, the residue yielded diffraction pattern in which all peaks could be indexed only to monoclinic BiVO_4 of JCPDS File NO. 75-2480. Absence of peaks due to any contaminant ascertains that the final residue is phase pure monoclinic BiVO_4 . In order to further differentiate whether it is monoclinic or tetragonal modification of scheelite, original ground mixture is heat treated at 500 °C for four hours and washed with distilled water a number of times after cooling.

XRD pattern of the heat treated sample is depicted in Fig. 1(c). Splitting of peaks at 35° and 46° in the XRD pattern confirm the phase as monoclinic in accordance with earlier reports in literature.

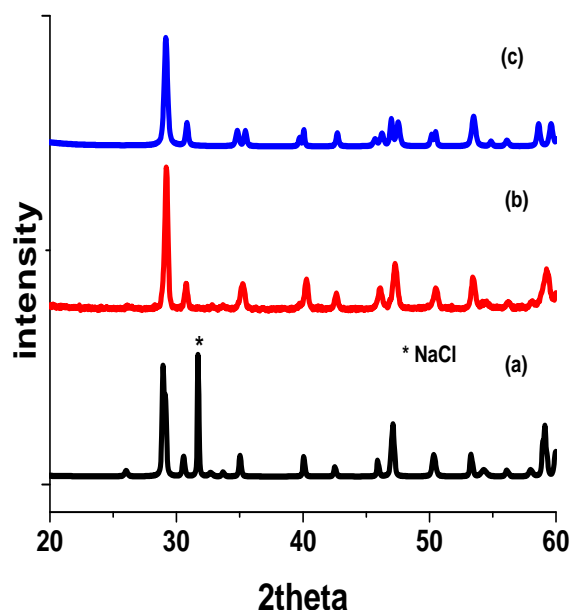


Figure 1: X-ray diffraction patterns of $\text{BiOCl} + \text{NaVO}_3$ mixture in 1:1 mole ratio after grinding (a) Before washing (b) after washing and (c) Heat treated at 500°C for 4hrs and washed.

Microstructural investigation using SEM revealed particle size less than 1 μm and particle agglomeration with no characteristic texture.

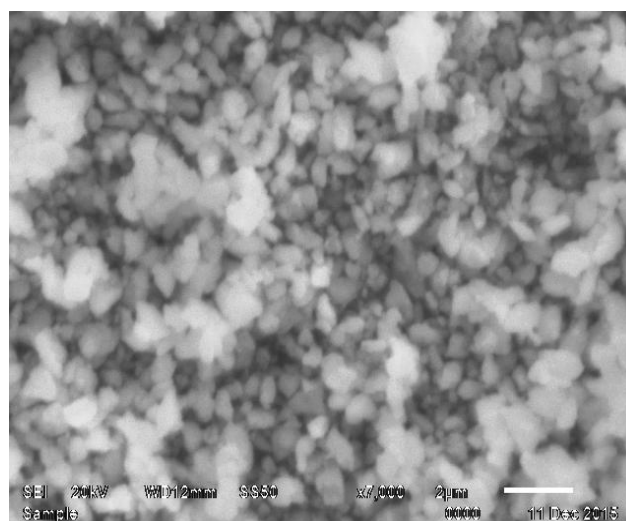


Figure 2: SEM image of BiVO_4 Photocatalyst.

Temporal variation of spectral contours of pure NB aqueous solution and NB aqueous solution containing 5 mg of BiVO_4 as a function of irradiation time are shown in Fig.3.

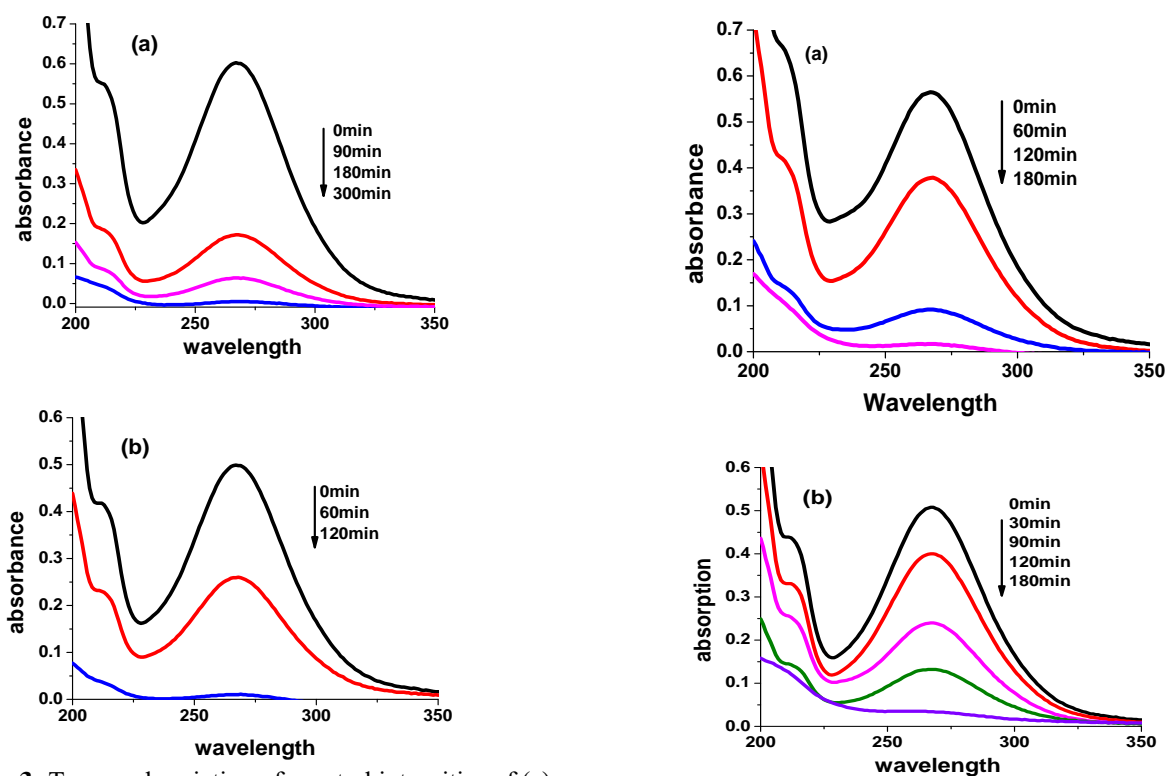


Figure 3: Temporal variation of spectral intensities of (a) aqueous solution of NB alone and (b) aqueous solution of NB containing 5mg BiVO₄ photocatalyst as a function of irradiation time.

From the figure, it can be seen that NB aqueous solution slowly undergoes photolysis in 300 min. but, in presence of 5mg BiVO₄, the spectral intensity decreases rapidly with progressive irradiation and attains near zero intensity for 120 min of exposure indicating that NB has completely photodegraded. In order to assess the effect of amount of catalyst, time dependent variation of spectral intensities are shown as a function of irradiation time in Fig. 4 for NB aqueous solution with different amounts (10, 20 and 30mg) of photocatalyst. It can be noticed that when the quantity of BiVO₄ is 10mg or 20 mg, time for complete degradation is 180min. while for 30mg BiVO₄, the extent of degradation is only 87% for 180 min of irradiation. Increase in photocatalyst lowered the extent of degradation. As the amount of catalyst increases the available active sites increase initially, but beyond a specific catalyst loading, the particles obstruct penetration of incident radiation and cause lowering of photocatalytic efficiency. Also, with increased load of catalyst there will be a tendency for the catalyst particles to agglomerate as a result of which the available surface for photo adsorption and desorption decreases. The data clearly indicates that 5mg photocatalyst is the optimum amount of photocatalyst.

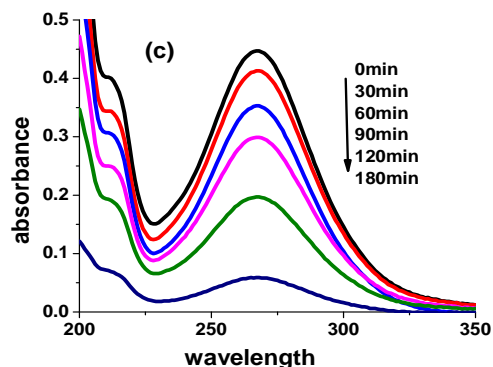


Figure 4: Variation of spectral intensities of NB as a function of irradiation time with (a) 10mg, (b) 20mg and (c) 30mg of BiVO₄.

The above results demonstrate that phase pure monoclinic BiVO₄ can be synthesized at room temperature by solid-state metathesis using BiOCl and NaVO₃ as reactants and aqueous nitrobenzene can be completely photodegraded over m-BiVO₄ under visible light. This method is more economical since visible light is used as irradiation source instead of U.V. radiation.

4. Conclusions

Phase pure monoclinic BiVO₄ is prepared by a facile room-temperature synthesis based on solid-state metathetic reaction between BiOCl and NaVO₃ as reactants. The formed product after washing was characterized by XRD and SEM. Photocatalytic degradation of nitrobenzene using synthesized BiVO₄ occurred for 120minutes of visible light irradiation without the use of either U.V. radiation or continuous oxygen or air bubbling.

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