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BiVO_4 nanoparticles: Preparation, characterization and photocatalytic activity

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Abstract: Bismuth vanadate (BiVO_4) nanoparticles were synthesized by a simple thermal decomposition method. The synthesized bismuth vanadate nanoparticles were characterized by X-ray diffraction analysis, it is found that the synthesized sample belongs to monoclinic BiVO_4 . Fourier transform infrared spectroscopy confirms the formation of Bi-O bond in the sample. Ultraviolet-Visible (DRS-UV-Visible) spectroscopy and photoluminescence spectroscopy reveal the optical property of the BiVO_4 nanoparticles. The morphology was identified by both scanning electron microscopy and high-resolution transmission electron microscopy. Further, the photocatalytic activity of BiVO_4 nanoparticles was investigated by photodegradation of methylene blue as a model organic pollutant.

Subjects: Environment & Agriculture; Physical Sciences; Soil Sciences

Keywords: bismuth vanadate; nanoparticles; visible light; methylene blue; photocatalyst

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PUBLIC INTEREST STATEMENT

Metal vanadate nanostructures have considerable attention by the materials scientists, due to their excellent applications in various fields. There are various methods have been developed for the synthesis of metal vanadate nanomaterials. However, production of metal vanadate nanostructures by thermal decomposition method is the best method to achieve particles with high surface area. Bismuth vanadate nanoparticles are used in the field of environmental remediation.

1. Introduction

Metal vanadate nanoparticles have considerable importance in various fields such as catalysis, photocatalysis, batteries, and implantable cardiac defibrillators (Crespi, Somdahl, Schmidt, & Skarstad, 2001; Konta, Kato, Kobayashi, & Kudo, 2003; Mai et al., 2010; Valeria & Floris, 2011). Among the various metal vanadate nanoparticles, an intense effort has been devoted to the synthesis and characterization of BiVO_4 , due to its unique properties such as ferroelasticity, optical, and conductivity (Sarkar & Chattopadhyay, 2012). It is used as gas sensor, solid-state electrolyte, and electrode for batteries and as yellow pigment (Smith, 2002). It is also used for water splitting, (Akihida, Yun, Yoshimi, Akihiko, & Rose, 2011) degradation of organic pollutant (Wenzong, Wenzhong, Lin, Songmei, & Ling, 2010), and O_2 evolution (Zhiqiang et al., 2011). In recent years, BiVO_4 has been considered as one of the important visible-light-driven photocatalysts (Lei et al., 2015). Monoclinic BiVO_4 with a moderate band gap (2.4 eV) exhibits the best photodegradation for pollutants like organic dyes and phenolic compounds under visible light irradiation. For instance, Kudo, Omori, and Kato (1999) first reported the photocatalytic activity of BiVO_4 . Wang et al. (2013) reported the methyl orange degradation behavior of BiVO_4 under visible light irradiation.

Different methods have been used for the preparation of BiVO_4 nanoparticles, like hydrothermal method, ultrasonic-assisted method, flame spray method, template-free solution method, and co-precipitation method (Dai et al., 2011; Karunakaran & Kalaivani, 2014; Kho et al., 2011; Kudo, Tokunaga, & Kato, 2001; Li et al., 2014). Among these methods, the thermal decomposition method has much attraction because of low cost, less time consumption, and good crystallized products with high homogeneity. It must be indicated that there are several reports about the synthesis and electrochemical properties of metal vanadate nanoparticles. However, we have selected a convenient thermal decomposition approach to synthesis BiVO_4 nanoparticles, and the photocatalytic activity of the nanoparticles was investigated.

In this paper, we report the simple thermal decomposition method for the preparation of bismuth vanadate (BiVO_4) nanoparticles. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-Visible, photoluminescence spectroscopy (PL), FE-SEM, and high-resolution transmission electron microscopy (HR-TEM) have been used to characterize the synthesized nanoparticles. Photocatalytic activity of BiVO_4 was examined by photodegradation of methylene blue (MB) under visible light illumination.

2. Experimental

2.1. Materials

Ammonium metavanadate (NH_4VO_3), bismuth nitrate, 1-dodecanol, and methylene blue were purchased from Sigma-Aldrich (AR) and used without any further purification.

Distilled water was used as solvent for all the experiments.

2.2. Experimental procedure

In order to prepare BiVO_4 nanoparticles, facile thermal decomposition method was adopted. To synthesis BiVO_4 , 0.1 mmol of ammonium metavanadate, 0.1 mmol of bismuth nitrate, and 1.0 mL of 1-dodecanol were mixed well with vigorously and the obtained gel was calcined at 450°C for 5 h (Sivakumar, Suresh, Giribabu, & Narayanan, 2015) in a muffle furnace. The obtained BiVO_4 nanoparticles were collected and subjected to further analysis.

2.3. Instrumentation

The structure and average crystallite size of BiVO_4 was analyzed by a Rich Siefert 3000 diffractometer with $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$). The M-O vibrations and impurity of BiVO_4 was analyzed by FTIR spectroscopy using a Shimadzu FTIR 8300 series instrument. One milligram of BiVO_4 was diluted with 100 mg of dried IR-grade KBr powder and subjected to a pressure of 10 tons to form pellet. The UV-Vis absorption spectrum of BiVO_4 was obtained on a CARY 5E UV-Vis-NIR spectrophotometer. The

fluorescence measurements were carried out on a Cary Eclipse FL1201M002 fluorescence spectrophotometer. Morphology and elemental analysis was analyzed by FE-SEM coupled with EDAX using a HITACHI SU6600 field emission scanning electron microscopy at an accelerating voltage of 30 kV. HR-TEM was recorded using a FEI TECNAI G² model T-30 at accelerating voltage of 250 kV. The prepared BiVO₄ nanoparticles were dispersed in acetone using ultrasonication and then required amount of dispersion was introduced on a carbon-coated copper grid, and were allowed to dry in air for HR-TEM analysis.

2.4. Photocatalytic experiment

The photocatalytic activity of BiVO₄ nanoparticles for the photodegradation of MB under visible light irradiation was performed at ambient condition. The experiment was conducted as follows: 0.05 g of BiVO₄ nanoparticles was dispersed into the aqueous MB solution (10⁻⁵ M, 100 mL) in a beaker. Prior to visible light irradiation, the suspension was stirred magnetically in dark for 20 min to reach adsorption-desorption equilibrium between BiVO₄ and MB dye. The mixture was then exposed to visible light irradiation under constant magnetic stirring. At regular intervals of 15 min, samples were collected and analyzed by a UV-Vis absorption spectrophotometer. The characteristic absorption peak of MB at about 664 nm was chosen for the photocatalytic degradation analysis.

3. Results and discussion

3.1. XRD analysis

Figure 1 presents powder XRD pattern of BiVO₄ nanoparticles synthesized by thermal decomposition method. All the XRD peaks can be readily indexed to monoclinic BiVO₄ (JCPDS No. 83-1699) (Gawande & Thakare, 2012). BiVO₄ has the lattice parameter value $a = 5.1956 \text{ \AA}$, $b = 5.0935 \text{ \AA}$, $c = 11.7045 \text{ \AA}$. No peaks due to impurity phases have been detected, indicating that the product is highly pure. It was observed that the diffraction peaks are narrow. The average crystallite size of the BiVO₄ nanoparticles was calculated as 39 nm using Scherrer formula,

$$D = K\lambda / (\beta \cos \theta)$$

where K is the shape factor, λ is the wavelength, β is the full width at the half-maximum of the line, and θ is the diffraction angle.

3.2. FTIR analysis

The FTIR spectrum of BiVO₄ nanoparticles (Figure 2) are matched with that of previously reported BiVO₄ (Mitev, Eriksson, Boily, & Hermansson, 2015). The band at 1,021 cm⁻¹ is attributed to the unshared V=O stretching vibrations. The bands at 833 and 706 cm⁻¹ are due to the antisymmetric stretching vibrations

Figure 1. XRD pattern of BiVO₄ nanoparticles.

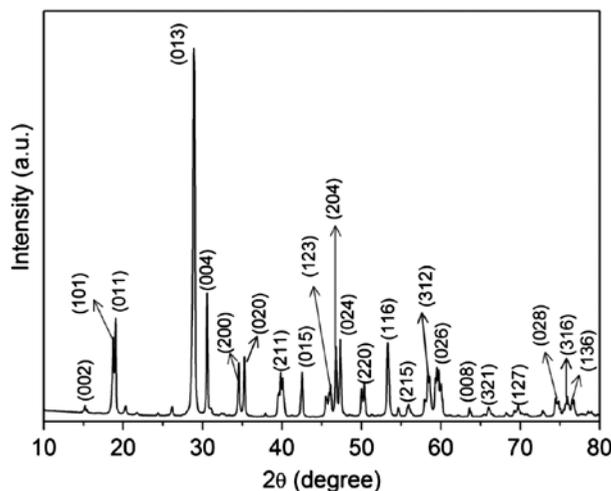
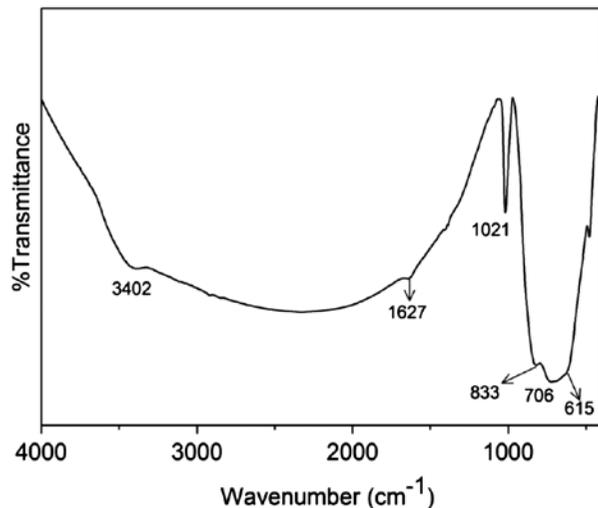


Figure 2. FTIR spectrum of BiVO₄ nanoparticles.



of the bound oxygen which are shared by two vanadium atoms (V–O–V) whereas a band at 615 cm⁻¹ is corresponding to the symmetric stretching mode of V–O–V units (Frost, Erickson, Weier, & Carmody, 2005). Furthermore, bands present at 3,402 and 1,627 cm⁻¹ are attributed to the O–H stretching and bending vibration of lattice water molecules (Hsiang & Yen, 2003).

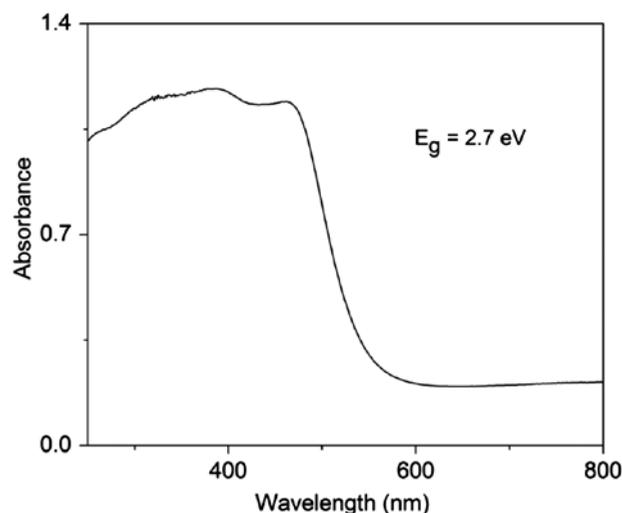
3.3. UV–Visible analysis

The optical absorption spectrum of the as-synthesized BiVO₄ nanoparticles is displayed in Figure 3. The two broad peaks in the range of 300–320 and 420–500 nm are due to ligand to metal charge transfer band (Gharbi et al., 1982). Essentially, the optical properties of nanoparticles are determined by their energy band. The optical bandgap (E_g) can be usually estimated using the following equation:

$$E_g \text{ (eV)} = 1240/\lambda$$

where λ is the wavelength of the light. The estimated band gap of the synthesized BiVO₄ nanoparticles is about 2.8 eV. Note that very few literatures reported the UV–Vis absorption of BiVO₄ nanostructures (Guisheng, Dieqing, & Jimmy, 2008).

Figure 3. DRS UV–Visible absorption spectrum of BiVO₄ nanoparticles.



3.4. PL analysis

PL spectroscopy is widely served to determine the information like existence of surface defects, oxygen vacancies, efficiency of charge-carrier trapping, and transfer in semiconductors (Sun, Dong, Wang, & Sun, 2009). This is attributed to the reason that the PL emission of BiVO_4 results from the recombination of photoexcited charges. The PL spectrum of BiVO_4 nanoparticles exhibits strong emission centered at 484 and 528 nm, respectively (Figure 4) which correspond to the recombination of the hole formed from the hybrid orbitals of Bi 6s and O 2p and the electron generated from the V 3d orbitals (Ma et al., 2012). It can be seen from Figure 4 that the emission bands of BiVO_4 have blue shift, in comparison with that reported for monoclinic BiVO_4 at 600 nm, which could be associated with the particle size and shape effects of the hydrothermally synthesized BiVO_4 sample (Lin et al., 2013).

3.5. Morphological analysis

The morphology of the as-prepared BiVO_4 was determined by scanning electron microscopy (SEM) and HR-TEM analysis. The SEM image of BiVO_4 nanoparticles is shown in Figure 5(a). It shows that the synthesized product is mostly in sphere like and plate-like particles. The energy dispersive spectroscopy (EDS) shows that the prepared sample consists of Bi, V, and O only (Figure 5(b)). Further quantitative analysis of EDS finds that the atomic ratio of Bi:V:O is about 1:1:4, indicating that a stoichiometric sample (Bi/V/O = 1:1:4) is obtained and is consistent with stoichiometric BiVO_4 , in agreement with XRD results. From the TEM images (Figure 5(c) and (d)), it can be seen that there are pores on the surface of the particles which mainly formed by the release of gaseous product from the interior of the precursor particles (Zhou, Tang, Zeng, & Qi, 2008).

3.6. Photocatalytic property

The photocatalytic activity of the semiconductor nanoparticles has been widely used to decompose various dye pollutants (Chen et al., 2008; Giribabu et al., 2012; Wu et al., 2010). Among them, BiVO_4 is one of the important photocatalyst for the degradation of dye effluents. Therefore, photocatalytic activity of the prepared BiVO_4 nanoparticles was measured with the photodegradation of MB under visible light irradiation. Figure 6 represents the absorption spectra of 1×10^{-5} MB solution during different irradiation times in the presence of BiVO_4 nanoparticles. Visible light irradiation of MB in the presence of BiVO_4 nanoparticles showed decrease in absorption maximum at 663 nm gradually without any significant peak shift. It suggests that the complete decolourization of aqueous MB was purely due to the BiVO_4 nanoparticles. Further, the absorbance showed a maximum value of 0.36 before visible light irradiation and decreased to a value of 0.01 after 105 min of visible light. Prolonged exposure of visible light to another 30 min did

Figure 4. PL emission spectrum of BiVO_4 nanoparticles.

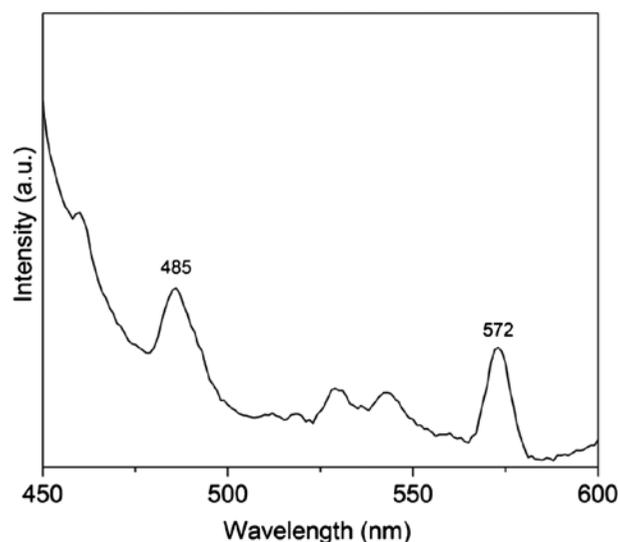


Figure 5. FE-SEM image (a), EDS spectrum (b), HR-TEM images of lower magnification (c) and higher magnification (d) of BiVO_4 nanoparticles.

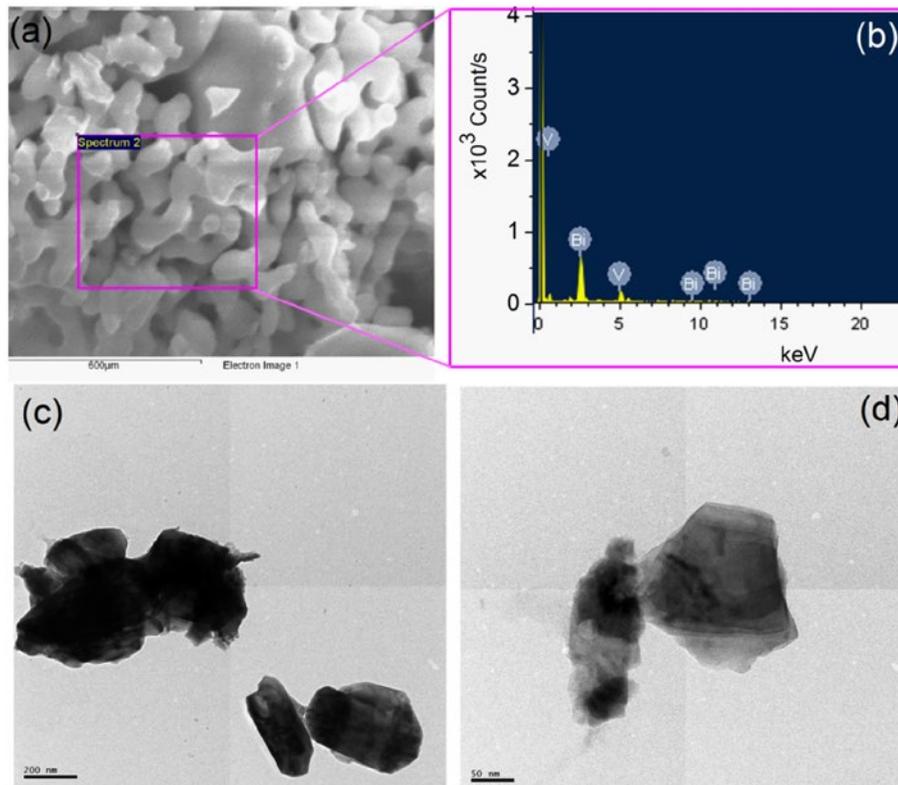
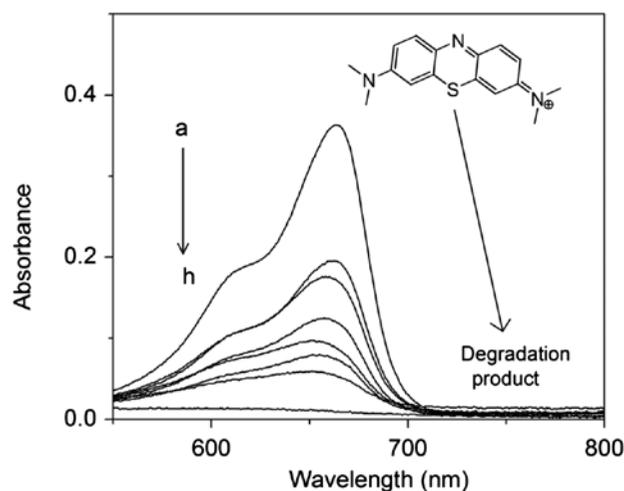


Figure 6. UV-Vis spectra of aqueous MB (1×10^{-5} M) at (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min (f) 75, (g) 90 min and (h) 105 min during photodegradation using BiVO_4 nanoparticles as photocatalyst.



not show any further decrease in the absorption maximum. Hence, the photodegradation efficiency was calculated with this value of absorbance and the degradation time of 105 min. The efficiency of decolourization was calculated using the equation.

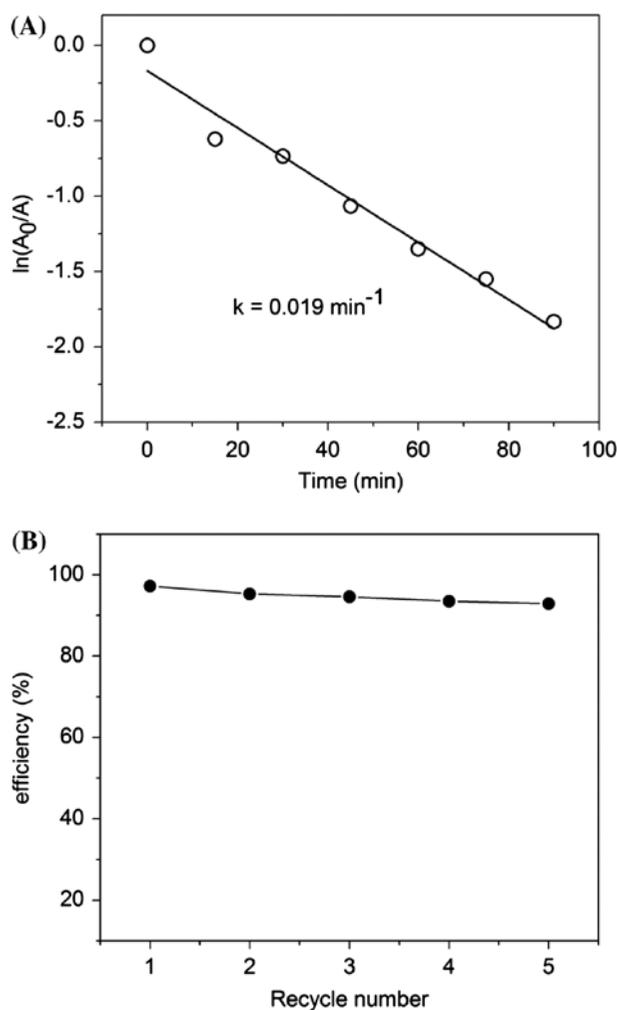
$$E = \frac{A(\text{MB})_0 - A(\text{MB})_\infty}{A(\text{MB})_0} \times 100$$

where $A(\text{MB})_0$ is the initial absorbance at $t = 0$ and $A(\text{MB})_\infty$ is the absorbance of MB after complete decomposition, $t = \infty$. The calculated decolourization efficiency is 97.2%. The photocatalytic performance of BiVO_4 nanoparticles is better or comparable with other photocatalysts for the photodegradation of MB

Table 1. Comparison of photodegradation behavior of some typical photocatalysts and the present BiVO₄ photocatalyst for the degradation of MB

Materials	Photodegradation efficiency (%)	Degradation time	Light source	References
ZnO/CdO	97.8	6 h	Visible light	Saravanan et al. (2011)
Bi ₂ S ₃ -TiO ₂ /polymer fiber composites	95.3	180 min	Solar irradiation	Ma et al. (2012)
Graphene wrapped BiVO ₄	95.0	210 min	Visible light	Gawande and Thakare (2012)
CdS nanorod	92.5	25 min	Visible light	Giribabu et al. (2012)
Ag/ZnO	92.0	8 h	Visible light	Whang et al. (2012)
BiVO ₄	97.0	105 min	Visible light	Present work

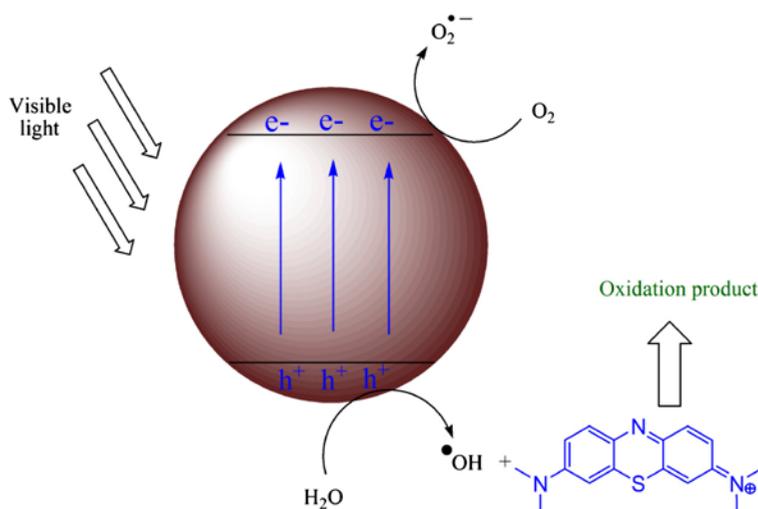
Figure 7. (A) In A vs. time graph of BiVO₄ for the photodegradation of MB. (B) Reusability of BiVO₄ for the photodegradation of MB.



(Table 1) (Ma et al., 2012; Saravanan, Shankar, Prakash, Narayanan, & Stephen, 2011; Whang, Hsieh, & Chen, 2012).

The photocatalytic degradation of MB at low concentration ($1 \times 10^{-5} \text{ M}$) can be generally a first-order reaction. According to the rate equation of first-order reactions:

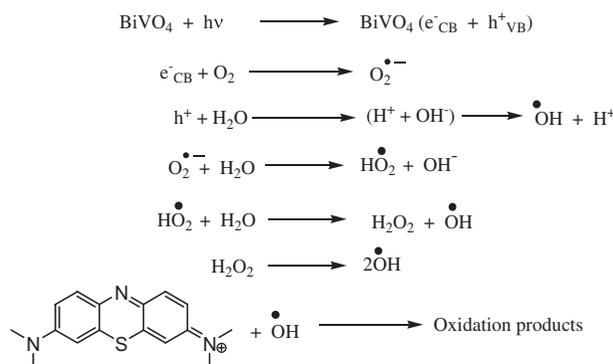
Scheme 1. Photocatalytic degradation mechanism of MB at the surface of BiVO₄ nanoparticles under the visible light irradiation.



$$\ln \left(\frac{A_t}{A_0} \right) = k_{app} t$$

where A_0 is the initial concentration of MB, A_t is the concentration of MB after a reaction time of t , and the k_{app} is a rate constant. Calculated rate constant of BiVO₄ is $k = 0.019 \text{ min}^{-1}$ as shown in Figure 7(A). Therefore, BiVO₄ possesses superior photocatalytic activity. Furthermore, recyclability of the photocatalyst is an important feature to judge the property of a photocatalyst for practical applications. To investigate the recyclability, BiVO₄ photocatalyst used is collected by centrifugation, washed by ethanol, and dried at room temperature. The recyclability of BiVO₄ nanoparticles is shown in Figure 7(B), which indicates that BiVO₄ maintains a similar level of photocatalytic activity even after five photocatalytic reaction cycles and thus has an excellent stability and reusability. The relative standard deviation for six successive reusability experiments was about 2.2%, indicating an excellent reproducibility.

BiVO₄ nanoparticles exhibit better photodegradation efficiency toward the MB within 60 min by visible light irradiation. When irradiating BiVO₄ nanoparticles with visible light, the photogenerated electrons (e^-) are ejected from valence-band (VB) to conduction-band (CB), generating holes (h^+) in VB. The photogenerated holes can react with adsorbed water on the surface of the BiVO₄ nanoparticles to generate highly reactive hydroxyl radical (OH^\bullet), whereas O_2 acts as an electron acceptor to form a superoxide anion radical ($\text{O}_2^{\bullet-}$). Further, the $\text{O}_2^{\bullet-}$ can act as an oxidizing agent or as an additional source of OH^\bullet . These reactive radicals have strong oxidizing ability and are able to degrade the MB dye into non-toxic organic compounds (Scheme 1) (Martínez-de la Cruz & Pérez, 2010). The possible photocatalytic reaction mechanism BiVO₄ is shown below.



4. Conclusions

In conclusion, synthesis of BiVO₄ nanoparticles with high yields through simple thermal decomposition method was described. The XRD and FTIR spectroscopy confirms the formation of monoclinic BiVO₄. The optical absorption property was studied by UV-Visible and PL spectroscopy. The photocatalytic activity of BiVO₄ nanoparticles was examined using MB as a model organic pollutant. The monoclinic BiVO₄ shows a photocatalytic efficiency of 97.2% for the degradation of MB under visible light irradiation in 105 min. Furthermore, the monoclinic BiVO₄ photocatalyst still maintains high stability up to 93% for MB degradation after five recycles.

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