

Application of BiVO₄ Nanocomposite for Photodegradation of Methyl Orange †

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Abstract: In this work, BiVO₄–graphene photocatalyst was prepared by a facile one-step hydrothermal method and characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The photocatalytic activity of this compound was investigated by destruction of methyl orange (MO) under visible light irradiation. The photodegradation results show that the prepared BVG compound has higher photocatalytic activity than the pure BiVO₄ compound. This compound can degrade 98% of MO under visible light irradiation. This work indicates that BiVO₄ compounds are excellent compounds for pollutant degradation under visible light irradiation.

Keywords: nanocomposite; BiVO₄; photodegradation; methyl orange

1. Introduction

The development of semiconductor photocatalysts for the degradation of organic pollutants under visible light irradiation is a challenging and necessary topic. In recent years, semiconductor photocatalysts have attracted great attention due to their potential applications in water splitting and organic pollutant photodegradation [1]. To date, TiO₂ as a useful material for many photocatalytic reactions has been intensively investigated. However, its application is limited by its wide band gap (3.2 eV) which requires ultraviolet irradiation for photocatalytic activation [2,3]. Therefore, developing alternative materials that are capable of using solar energy has become one of the most challenging topics today. Great efforts have been exerted to develop visible-light-responsive photocatalysts for the degradation of dyes. Various semiconductor photocatalysts, such as WO₃, ZnO, BiVO₄, and CdS, have been investigated for the photocatalytic degradation of water pollutants under visible light irradiation [4].

Among the photocatalysts investigated in these works, BiVO₄ is an attractive semiconductor with three crystalline phases: tetragonal zircon-type (z-t), tetragonal sheelite-type (s-t), and monoclinic sheelite-type (s-m). Monoclinic BiVO₄ is generally considered to be more active than the other phases [5]. BiVO₄ is nontoxic and chemically stable in aqueous solution, and the narrow band gap (2.4 eV) of BiVO₄ can provide effective utilization of the visible light region [6].

Graphene materials have shown great potential as catalysts in the photocatalysis process in recent years. Its unique properties such as 2D structure, high mobility of charge carriers, theoretically large surface area (~2600 m²/g), etc., have made graphene as a prospective candidate for the design of photocatalytically active composites [7,8].

In this work, we synthesized monoclinically structured BiVO_4 and BiVO_4 -graphene compound. The photocatalytic activities of the prepared samples were evaluated by methyl orange decomposition under visible irradiation.

2. Experimental

2.1. Synthesis of Bismuth Vanadate

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 mmol, 0.485 g) was dissolved in 20 mL of 1 M HNO_3 by stirring for 30 min at room temperature. An alkaline solution of NH_4VO_3 was prepared by dissolving 0.117 g (1 mmol) of NH_4VO_3 in 20 mL of 0.5 M NaOH under stirring for 30 min at room temperature. The NH_4VO_3 solution was added dropwise to the $\text{Bi}(\text{NO}_3)_3$ solution with stirring to get a clear solution. The resultant solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, sealed, and heated at 120 °C for 24 h under autogenous pressure. The obtained samples were filtered and washed with deionized distilled water followed by absolute ethanol. Finally, the obtained solid samples were dried in a hot air oven [9].

2.2. Preparation of the BiVO_4 -Graphene Nanocomposite

The prepared solution was named A. A facile one-step solvothermal method was used to synthesize the BiVO_4 -graphene nanocomposite by dissolving 0.5 wt % of graphene. Then, 0.485 g of the prepared BiVO_4 powder was added into solution A. The suspensions were then transferred into a 100 mL Teflon-sealed autoclave and kept at 120 °C for 24 h. The resulting products were recovered by centrifugation, rinsed with DI water and ethanol, and dried at 60 °C for 6 h in a hot air oven.

3. Results and Discussion

3.1. X-ray Powder Diffraction

The XRD pattern of the prepared BiVO_4 -graphene nanocomposite is shown in Figure 1. The characteristic peak of graphene is at $2\theta = 25^\circ$. In the XRD pattern of the BiVO_4 -graphene photocatalyst, the broad peak of graphene is observed at $2\theta = 25^\circ$. Due to the high crystallinity of BiVO_4 and, subsequently, its sharp peaks, the intensity of the graphene peak is low. Due to the high purity of the synthesized samples, no impurity peaks are observed in the X-ray diffraction pattern of this compound.

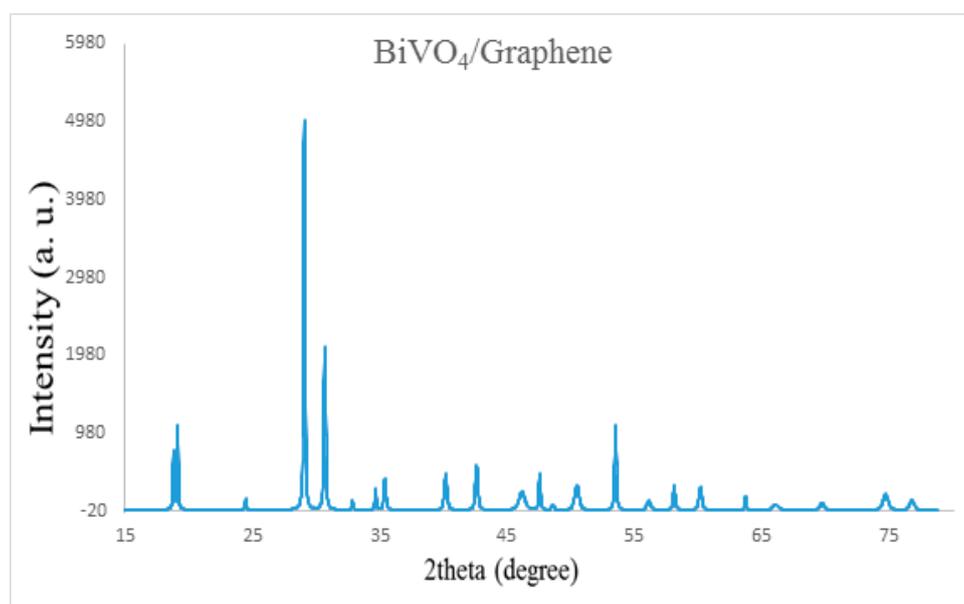


Figure 1. The XRD pattern of the prepared BiVO_4 -graphene nanocomposite.

3.2. DRS Analysis of the Prepared Sample

The DRS analysis of the prepared sample is shown in Figure 2. Based on the DRS analysis, the band gap of BiVO_4 was calculated as 2.47 eV. Graphene with its high charge mobility can decrease the recombination parameter and decrease the band gap, consequently increasing the photocatalytic activity.

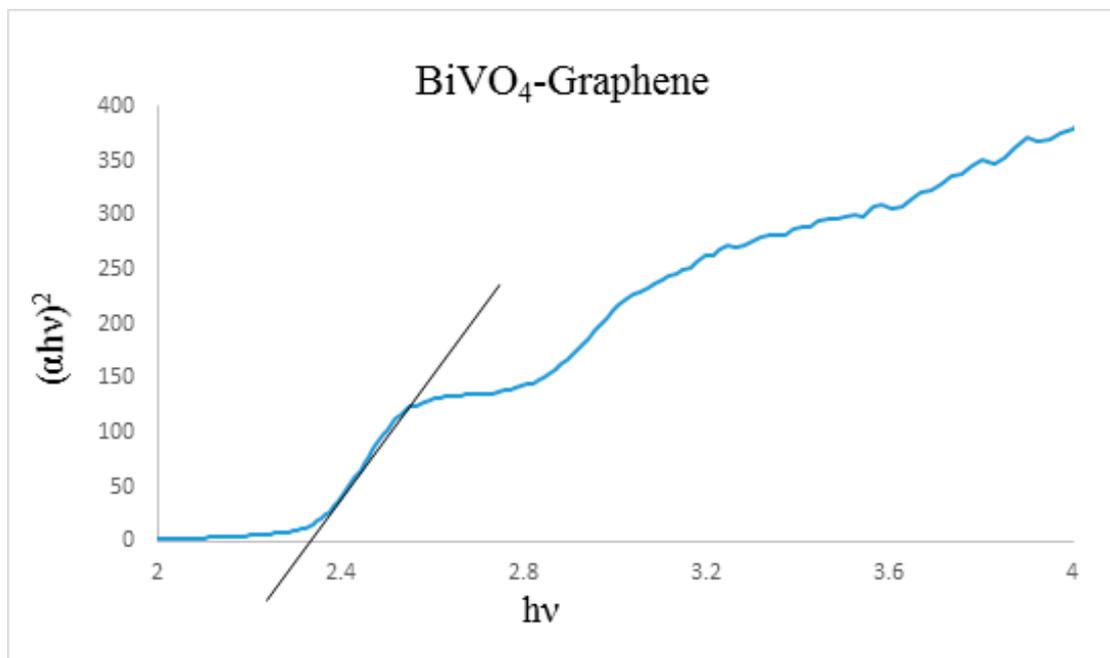


Figure 2. DRS analysis of the prepared BiVO_4 -graphene nanocomposite.

3.3. Morphological Characterization

A SEM image of the BiVO_4 -graphene sample is shown in Figure 3. The sheet-like morphology of the BiVO_4 -graphene sample is obvious in the SEM image of this compound. Due to the sheet-like morphology of the graphene plates, the BiVO_4 plates decorated on the graphene sheets arrange in the sheet-like morphology.

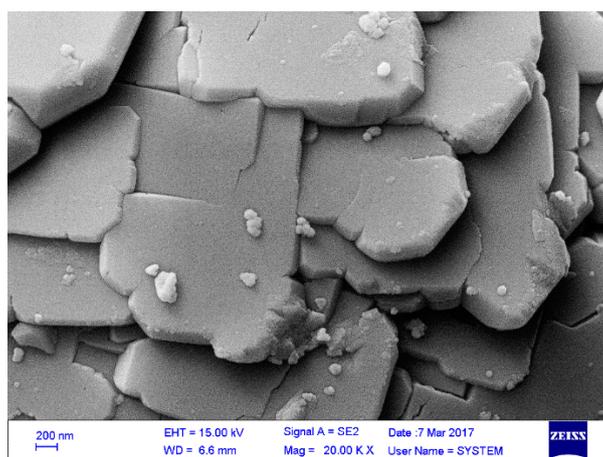


Figure 3. Cont.

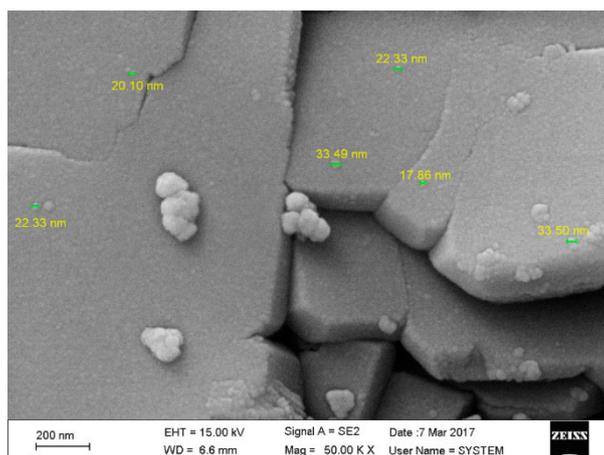


Figure 3. SEM image of the prepared BiVO₄-graphene compound.

3.4. IR Spectrum of the Prepared Sample

The IR spectrum of BiVO₄-graphene is shown in Figure 4. In this IR spectrum, the strong and broad peak at 1261 cm⁻¹ is in response to the BiVO₄ vibrational system.

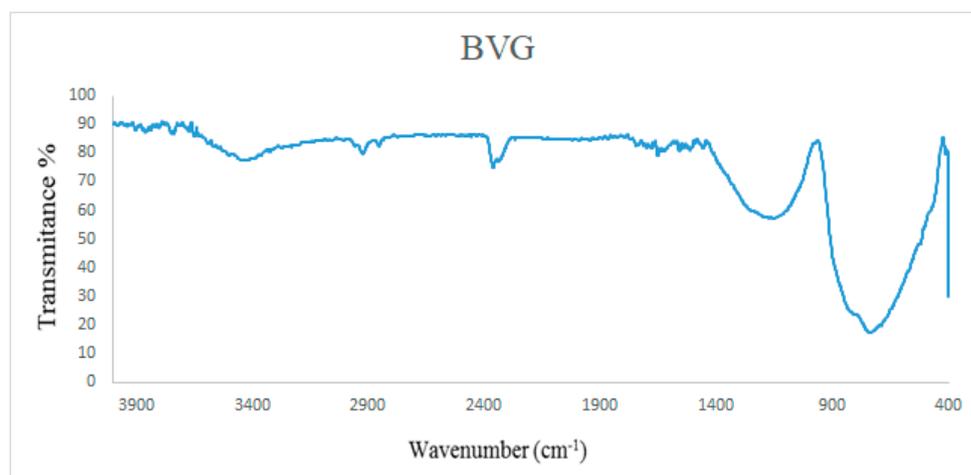


Figure 4. IR spectrum of the prepared BiVO₄-graphene sample.

3.5. Photocatalytic Activity of the Prepared Samples

The photocatalytic activity of BiVO₄ and BiVO₄-graphene samples was evaluated by the degradation of methyl orange in aqueous solution (10 ppm) under visible light irradiation. As shown in Figure 5, under visible light irradiation, 69% of the methyl orange dye was destroyed in the presence of the BiVO₄ sample after 240 min, and 98% of the methyl orange dye was destroyed in the presence of the BiVO₄-graphene sample after 180 min. The results showed that the BiVO₄-graphene nanocomposite has higher photocatalytic activity than pure BiVO₄.

In the BiVO₄-graphene nanocomposite, electron-hole pairs are generated after excitation of BiVO₄ with visible light irradiation. Due to the low band gap of BiVO₄, this low-power visible light is sufficient to excite the BiVO₄ photocatalyst. One of the important parameters of photocatalysis reactions is the recombination process. This especially happens in the low-band-gap semiconductors. The recombination process decreases the efficiency of the photocatalytic reactions. In a BiVO₄-graphene nanocomposite, due to the presence of graphene, the prepared electron-hole pairs move to graphene and reach the photocatalyst surface. Therefore, the recombination process is reduced in the photocatalytic reaction of this nanocomposite.

The high charge conductivity of graphene increases the migration of charges to the photocatalyst surface. The synergistic effect between graphene and BiVO₄, proper adjustment between the valence

and conduction bands of graphene and BiVO₄, and proper composition between these two components yield the high photocatalytic activity of the prepared BiVO₄-graphene nanocomposite.

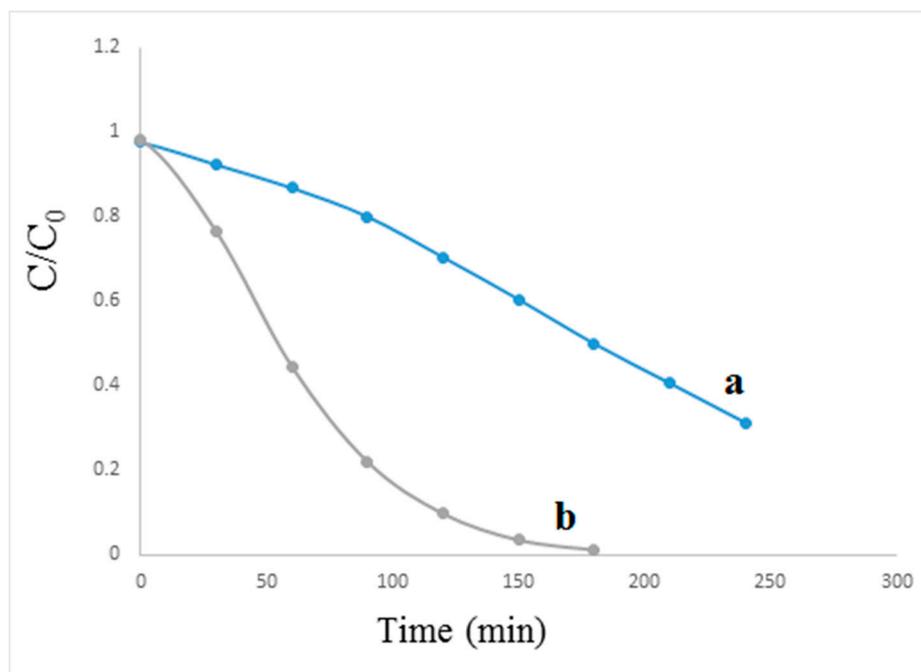


Figure 5. The photodegradation results of methyl orange (MO) over (a) BiVO₄ and (b) BiVO₄-graphene nanocomposite under visible light irradiation.

4. Conclusions

In this work we prepared BiVO₄ and BiVO₄-graphene via a simple hydrothermal method. The photocatalytic activity of the prepared BiVO₄ is low due to the low band gap of this compound. The occurrence of the recombination process is high in BiVO₄. The photodegradation results show that the composition of graphene and BiVO₄ effectively increases the photocatalytic activity of the prepared photocatalyst. Thus, the recombination process of BiVO₄ decreases after composition with graphene.

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References

1. Lee, S.Y.; Park, S.J. TiO₂ photocatalyst for water treatment applications. *J. Ind. Eng. Chem.* **2013**, *19*, 1761–1769.
2. Woan, K.; Pyrgiotakis, G.; Sigmund, W. Photocatalytic carbon- nanotube-TiO₂composites. *Adv. Mater.* **2009**, *21*, 2233–2239.
3. Chang, S.M.; Liu, W.S. Surface doping is more beneficial than bulk doping to the photocatalytic activity of vanadium doped TiO₂. *Appl. Catal. B: Environ.* **2011**, *101*, 333–342.
4. Chen, D.; Ye, J. Hierarchical WO₃ hollow shells: dendrite, sphere, dumbbell, and their photocatalytic properties. *Adv. Funct. Mater.* **2008**, *18*, 1922–1928.
5. Zhao, Y.; Li, R.; Mu, L.; Li, C. Significance of crystal morphology controlling in semiconductor-based photocatalysis: A case study on BiVO₄ photocatalyst. *Crystal Growth Des.* **2017**, *17*, 2923–2928.
6. Wang, Y.; Wang, W.; Mao, H.; Lu, Y.; Lu, J.; Huang, J.; Ye, Z.; Lu, B. Electrostatic self-assembly of BiVO₄-reduced graphene oxide nanocomposites for highly efficient visible light photocatalytic activities. *ACS Appl. Mater. Interfaces* **2014**, *6*, 12698–12706.
7. Katsnelson, M.I. Graphene: Carbon in two dimensions. *Mater. Today* **2007**, *10*, 20–27.

8. Rao, C.; Biswas, K.; Subrahmanyam, K.; Govindaraj, A. Graphene, the new nanocarbon. *J. Mater. Chem.* **2009**, *19*, 2457–2469.
9. Rahimi, R.; Mehrehjedy, A.; Zargari, S. BiVO₄/Mn₂O₄ a novel p–n heterojunction photocatalyst functionalized with metalloporphyrins: Synthesis, charge transfer mechanism, and enhanced visible-light photocatalysis for degradation of dye pollutant. *Environ. Progress Sustain. Energy* **2017**, *36*, 1439–1448.



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