Synthesis and Photocatalytic Application of $BiVO_4$ Nanocrystalline Functionalized by porphyrin with Two Different Crystalline Phases as an Efficient Photocatalyst

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Abstract

A series of different Nanocrystalline phases, Bismuth vanadate ($BiVO_4$) (photocatalysts monoclinic/tetragonal heterophase) and $BiVO_4$ Nanocrystalline functionalized by porphyrin, have been prepared. The prepared sample was characterized by powder X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy (FT-IR). Photocatalytic activities samples were evaluated by the methyl orange decomposition under visible and UV light irradiation. The degradation was observed by the decrease in the absorbance peak studied with UV-Vis spectrophotometer.

Keywords: Porphyrin, Bismuth vanadate, Photocatalytic, Nanocrystalline,

1. Introduction

Porphyrins as a supermolecular compound and primary chromophores in photosynthesis, are nature's light harvesting system [1]. Porphyrins capture a broad range of the solar spectrum due to their strong absorption band in both visible and near infrared regions [2]. Heterogeneous photocatalytic oxidation, using semiconductors, has attracted great interest as a promising technology for the purification of contaminated water [3-6]. Among the various semiconductor photocatalysts, TiO_2 has been used widely, but some disadvantage of this photocatalyst limits its applications [7]. Thus, investigations have been concentrated on the design and development of other metal oxides properties of photoinduced charge separation under excitation light illumination. Among several studies of oxides with activity, under visible-light irradiation, $BiVO_4$ has received special attention [8, 9]. There are three crystalline phases reported for $BiVO_4$: tetragonal zircon (z-t), monoclinic scheelite (s-m) and tetragonal scheelite (s-t) [10]. Bismuth vanadate ($BiVO_4$) has been recognized as a strong photocatalyst (band gap: 2.4 eV) for pollutant decomposing, due to its photocatalytic response to the visible-light region and relatively strong oxidation properties for water purification [11]. In this work, we synthesized mixed monoclinic and tetragonal structure of $BiVO_4$ and $BiVO_4$-TCPP via a simple chemical method. Photocatalytic activities of samples were evaluated by the methyl orange decomposition under visible and UV light irradiation. The present study has focused on the preparation of catalyst with high photocatalytic activity. The results show that the presence of interface in monoclinic-tetragonal heterophase provides a special condition for charge transfer, increase the separation of photoinduced electron-hole pairs, and changes the migration direction of photoinduced carriers.

2. Experimental

2. 1. Synthesis of Bismuth Vanadate

In the present work, for the synthesis of bismuth vanadate ($BiVO_4$) with monoclinic-tetragonal phases, NH_4VO_3 and Bi $(NO_3)_3.5H_2O$ in equimolar aqueous solution was mixed. PEG was added to the solution including Bi $(NO_3)_3.5H_2O$, then the mixture was stirred for 1h and sonicated by ultrasonic for 30 min at room temperature. The yellow precipitate of $BiVO_4$ was separated from the solution by centrifuging and was washed with distilled water and ethanol. The final production was dried in the oven at 60˚C. The corresponding product was calcined at 450˚C for 120 min.

2. 2. Synthesis of porphyrin and $BiVO_4$ functionalized by porphyrin

Tetrakis (4-carboxyphenyl) porphyrin (TCPP) was prepared by refluxing 4-Carboxybenzaldehyde and pyrrole in propionic acid. In order to sensitize the $BiVO_4$ with porphyrin compounds, $BiVO_4$ and TCPP with 10:1 ratio was refluxed in the DMF solvent. After washing with DMF, the synthesized product obtained.

3. Results and discussion

3.1. Characterization

Figure. 1 shows the XRD patterns of $BiVO_4$ and $BiVO_4$-TCPP. Fig. 1a shows the $BiVO_4$ sample is a heterophase including tetragonal Zircon (z-t) and monoclinic scheelite (s-m) with the presence of peaks $2\theta = 24.4^\circ, 32.7^\circ$ (JCPDS no. 14-0133) for tetragonal zircon (z-t) structure and peaks of $2\theta = 28.8^\circ$ (JCPDS no. 14-0688) for monoclinic scheelite (s-m) structure. As Fig. 1b shows, the significant change have not seen in the XRD pattern of $BiVO_4$-TCPP compounds, therefor, in the $BiVO_4$ functionalized with porphyrin compounds, the distance between the plates of crystalline $BiVO_4$ and its structure was not changed.

The representative SEM images of the prepared $BiVO_4$ and $BiVO_4$-TCPP composites are shown in Fig. 2. According to the image 2b, the presence of TCPP did not change morphology of $BiVO_4$.

The diffuse reflectance spectra (DRS) of the synthesized samples are shown in Fig. 3. These results have been indicated that the porphyrin sensitization had great effect on the photocatalytic activity of $BiVO_4$ in visible light. DRS analysis is an important method for investigation of the functionalization of metal oxide with the porphyrin compounds. As Fig. 3 shows, the sensitization of $BiVO_4$ by porphyrin change the absorption edge of $BiVO_4$.

Fourier transform infrared spectroscopy (FT-IR) were shown in Fig. 4. Moreover, the bands at 700–800 cm^{-1} for both samples, pure $BiVO_4$ and $BiVO_4$ composite, were associated with the bending vibration of the VO_4^{3-}.

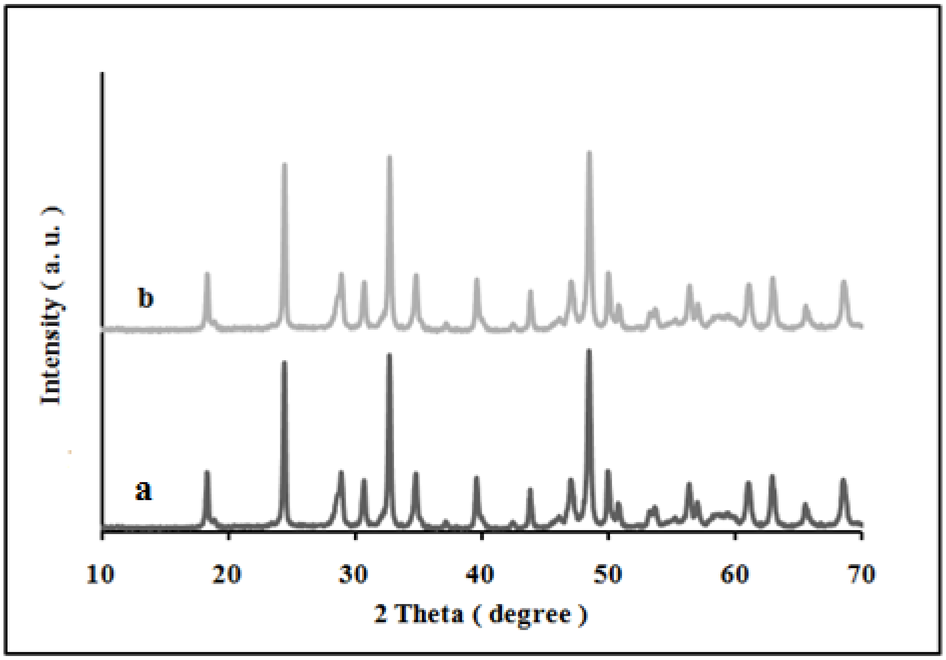

Fig. 1. XRD pattern of a) mixed monoclinic and tetragonal structure of prepared $BiVO_4$, b) $BiVO_4$-TCPP.

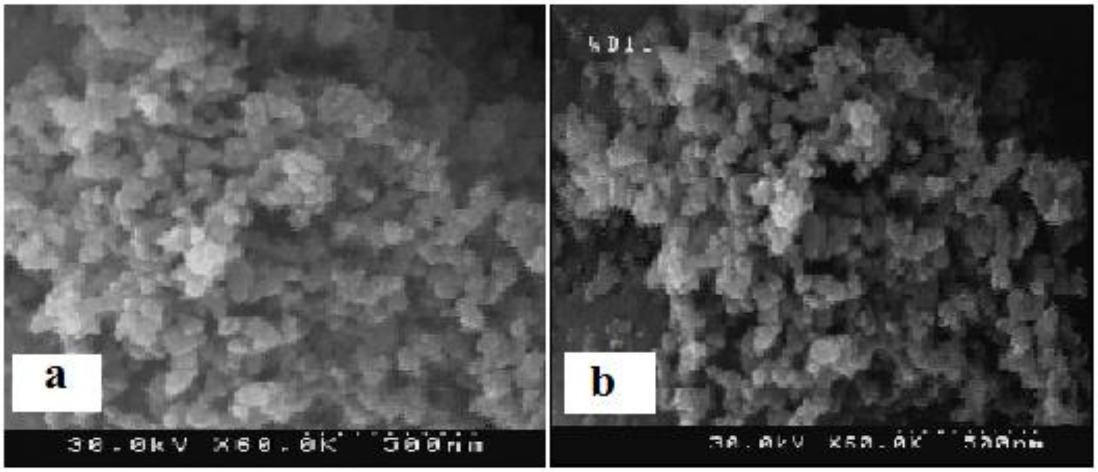

Fig. 2. SEM images of a) pure $BiVO_4$ and b) $BiVO_4$-TCPP.

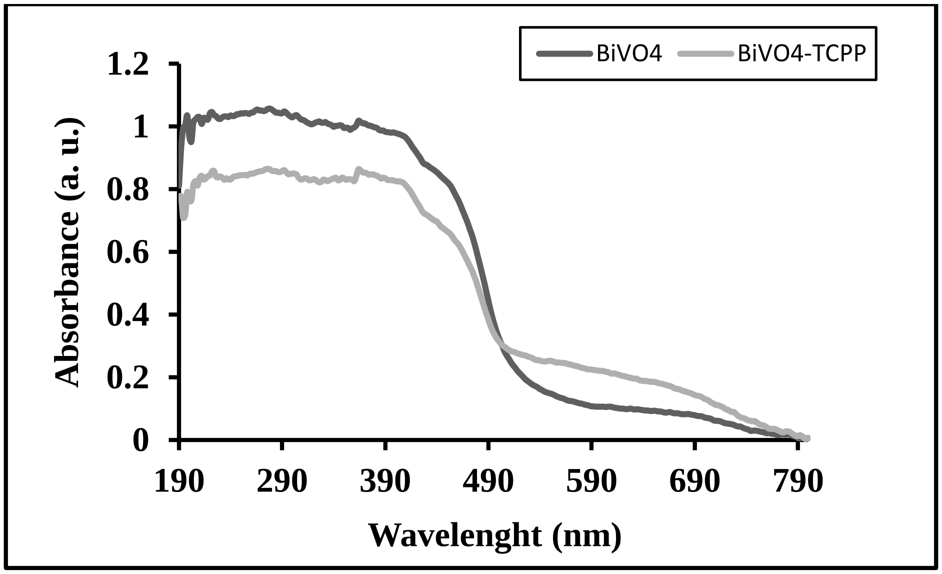

Fig. 3. UV–Vis diffusion reflectance spectra of pure $BiVO_4$ and $BiVO_4$-TCPP.

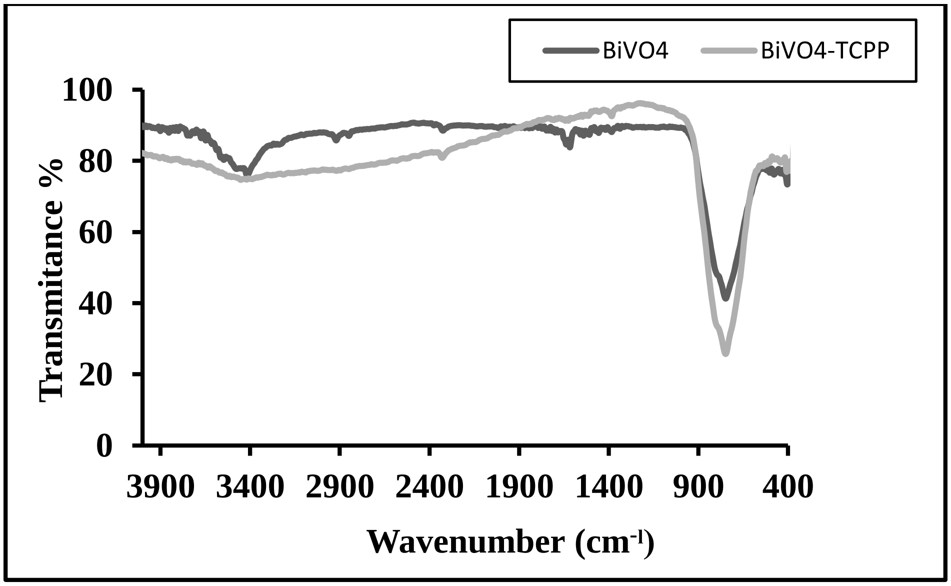

Fig. 4. FT-IR spectra of pure $BiVO_4$ and $BiVO_4$-TCPP.

3.2 Photocatalytic Activity of Prepared Samples

The photocatalytic activity of $BiVO_4$ sample was evaluated by the degradation of methyl orange in the aqueous solution (10 ppm) under the visible light and UV light irradiation. As shown in Fig. 5, under the irradiation of UV light ($\lambda > 400$ nm), 25% of the methyl orange dye was destructed in the presence of the $BiVO_4$ sample after 240 min, which was higher than the irradiation of visible light. The result showed that under the irradiation of visible light, 47% of the methyl orange dye was destructed in the presence of the $BiVO_4$-TCPP sample after 240 min.

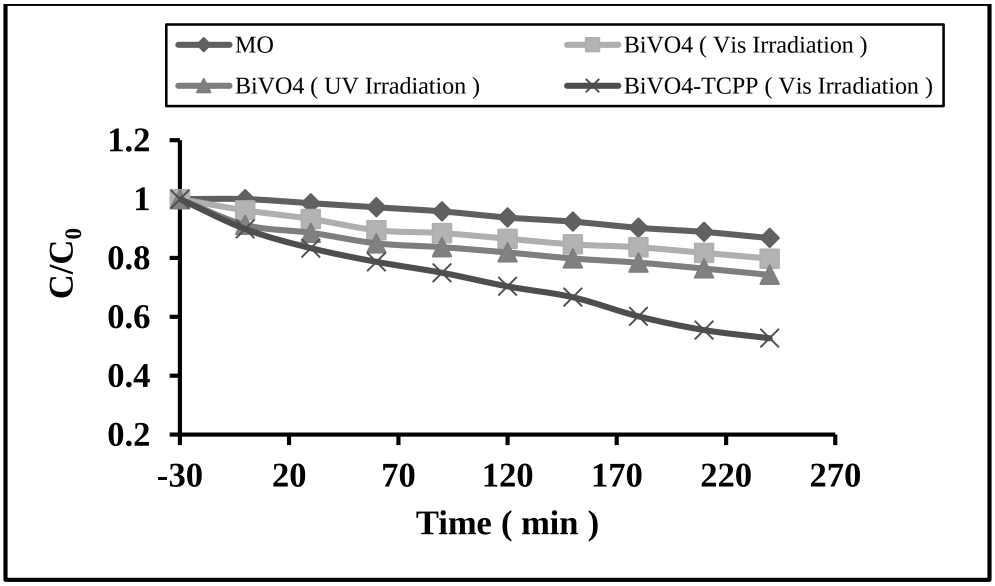

Fig. 5. Photodegradation of MO using pure $BiVO_4$ and $BiVO_4$-TCPP.

3. Conclusions

In tetragonal/monoclinic heterophase $BiVO_4$, a tight interface junction has been formed between $BiVO_4$ (s-m) and $BiVO_4$ (z-t) in a nanosize level. Monoclinic scheelite $BiVO_4$ (s-m) was mainly formed at the surface of heterophase $BiVO_4$ nanoparticles after calcination. Tetragonal/monoclinic heterophase $BiVO_4$ has higher photocatalytic activity under the irradiation of UV light. The new $BiVO_4$-TCPP photocatalyst was successfully prepared through a simple method. As expected, the new $BiVO_4$-TCPP not only has high photodegradation efficiency than the pure $BiVO_4$, but also excellent photostability for the photodegradation of MO under visible light irradiation. This is because the energy level of the excited TCPP and the conduction band of $BiVO_4$ was properly overlapped which leads to decrease the recombination of the electron–hole pair and thus promotes the photodegradation efficiency.

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