Synthesis of pineapple slab like morphology of ternary BiVO_4 /graphene/porphyrin nanocomposite with enhanced visible light photocatalytic activity

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Abstract

In this work, composites of BiVO_4 with different contents of graphene are synthesized. Photocatalytic investigations determine that the prepared BiVO_4 -graphene (BVG) nanocomposite with 0.5% of graphene has higher photocatalytic activity among the synthesized nanocomposites. The photocatalytic efficiency of BVG is 2 times higher than BiVO_4 . To improve the photocatalytic activity under visible light irradiation, the prepared nanocomposite was photosensitized with porphyrin as strong light harvesting agent. The obtained BVG photosensitized with porphyrin (BVG-P) could completely remove methyl orange dye in 180 min. Slab-like morphology and the incorporation of porphyrin show to be key factors in high photocatalytic activity of BVG-P.

Keywords Graphene · BiVO_4 · Porphyrin · Photocatalysis · Visible light

1 Introduction

With the rapid development of industry, pollutant removal from waste waters is a major concern in recent years [1, 2]. With regard to the problem of fuel resources, sunlight can be used as a renewable and abundant source of energy and photocatalytic processes seem to be very promising in harvesting sunlight energy [3, 4]. One example is, water purification semiconductor photocatalysts, in which, the photocatalyst is excited under light irradiation, which leads to the formation of radical species such as $\text{OH}^\cdot$ and $\text{O}_2^\cdot$. These highly reactive radicals then oxidize pollutant molecules [5, 6].

In our previous studies, we have investigated the photocatalytic activity of the $\text{BiVO}_4/\text{Mn}_3\text{O}_4$ heterojunction catalyst [7]. Its high photocatalytic activity in the degradation of MO under the irradiation of the low-power visible light, led us to investigate the potential of BiVO_4 further. Bismuth vanadate exists in three crystalline phases: monoclinic

scheelite (s-m), tetragonal scheelite (s-t) and tetragonal zircon (z-t) structures. Studies show that monoclinic scheelite (s-m) BiVO_4 exhibits the highest photocatalytic activity, under the visible light irradiation. BiVO_4 is a semiconductor with 2.4–2.9 eV band gap. Added to its excellent photocatalytic properties, BiVO_4 is also non-toxic and chemically stable [8–11]. The photocatalytic properties of BiVO_4 strongly depend on its morphology. BiVO_4 with closer to flat-shaped morphologies, have been known to be more efficient photocatalysts under the visible light irradiation [12]. Here, as expected, BVG-P with slab-like morphology also possesses optimal photocatalytic properties.

The electron-hole recombination is an important factor that determines the efficiency of a photocatalyst [13]. The decrease of the electron-hole recombination in BiVO_4 , leads to an increase in its photocatalytic efficiency [14]. Several methods have been employed to decrease the electron-hole recombination in semiconductors and incorporating them into composites has proved to be an

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effective approach [15, 16]. Graphene with a 2D structure and high surface area is also known to have a high mobility of charge carriers and this makes it a suitable candidate for making composites with BiVO_4 [17–19].

Enhancing a photocatalysts activity in the visible region of the electromagnetic field, instead of higher energy ultraviolet region, is an ongoing challenge [20]. One useful strategy is to photosensitize the photocatalyst by a light harvesting agent, such as porphyrins. For example, porphyrins are used in dye sensitized solar cells and photodynamic therapy. Porphyrins characteristic peaks cover a wide range of UV–Vis spectrum from 300 to 800 nm, including a sharp peak in nearly 300 nm, also known as sorlet band, and four Q peaks in the range of 500–800 nm [21–23].

In this study, a composite based on BiVO_4 , graphene and porphyrin is synthesized. The slab-like morphology and graphene enhance electron–hole recombination and photocatalytic properties and porphyrin is mainly responsible for an improved visible light absorption of the photocatalyst. A previous survey among porphyrin molecules with different substituents, suggest that a carboxylic acid groups, makes the porphyrin a better sensitizer [24].

2 Materials and methods

2.1 Materials

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, NH_4VO_3 , nitric acid, sodium hydroxide, terephthalaldehydic acid, pyrrole, propionic acid, solvents such as N,N-dimethylformamide (DMF), and ethanol, were purchased from Merck. All reagents and solvents were used without further purification. Graphene oxide was synthesized according to a previous report [25].

2.2 Instrumentation

X-ray diffraction (XRD) analysis was conducted on a Philips (PW1800, Netherlands) using Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Fourier transform infrared (FTIR) spectra were recorded by a FTIR-8400S spectrophotometer (Shimadzu, Japan) in the range of 400–4000 cm^{-1} . Scanning electron microscopy (SEM) was performed on a Zeiss (SIGMA VP-500, Germany) microscope operating. EDS analysis was conducted using England, Oxford Instrument. The ultraviolet–visible (UV–Vis) diffusive reflectance absorption spectra (DRS) of the samples were obtained using a Shimadzu MPC 2200 spectrophotometer. UV Vis spectra were obtained on a double beam Shimadzu (UV 1700, Japan) spectrophotometer. The lamp used in this work was a 40 W white LED (VF: 15 18 V, IF: 300 MA, TC: 600 8500 K).

2.3 Photocatalytic test

Photocatalytic activities of the prepared samples were determined by the degradation of MO in aqueous solutions, under visible light irradiation. The 40 W white LED lamp was used as the visible light source. Experiments were performed at room temperature as follows: 0.05 g of photocatalyst was added to 50 mL of MO (10 mg/L) aqueous solution. Before irradiation, the mixture was first kept in the dark for 30 min to reach the adsorption–desorption equilibrium under magnetic stirring [3, 26]. At the same irradiation time intervals, samples were taken from the suspension and immediately centrifuged. Then the concentration of MO was determined using an UV–Vis spectroscopy.

2.4 Preparation of the BiVO_4 –graphene nanocomposite

BiVO_4 was synthesized using a modified hydrothermal procedure at 120 °C for 24 h [7]. To prepare the BVG composite, graphene Oxide (GO) was first prepared using graphite by Hummer's method [27]. The GO was exfoliated to yield a brown dispersion after ultrasonication. The prepared suspension was named A. A one-step solvothermal method was used to synthesize the BVG nanocomposite by dissolving different mass ratios of GO to achieve the nanocomposite with 0.2, 0.5, 1, 3, 5 wt% of graphene. Then, 0.485 g of the prepared BiVO_4 powder was added to suspension A and the suspension was ultrasonicated until a homogeneous solution was resulted. Then, the suspensions were transferred into a 100 mL Tefon-sealed autoclave and was kept at 120 °C for 24 h. During the solvothermal reaction, both graphene oxide reduction and BiVO_4 loading were achieved. The resulting products were recovered by centrifugation, rinsed with DI water and ethanol, and was then dried at 60 °C for 6 h. The samples are named as BVG (0.2%), BVG (0.5%), BVG (1%), BVG (3%), BVG (5%), and percentages indicate the wt% of graphene.

2.5 Photosensitized of the Prepared BVG with Porphyrin

Tetrakis(4-carboxyphenyl)porphyrin (TCPP) was prepared according to the previous report [28]. For photosensitizing BVG, BVG sample with the optimum content of graphene and TCPP were refluxed in DMF for 6 h (BVG: TCPP, weight ratio 10:1). The obtained product was named BVG-P. The prepared sample was used in the photocatalysis process under visible light irradiation, but BVG-P did not show much photocatalytic activity,

a higher concentration of TCP was used in the photosensitization process. There seems to be a threshold for maximum amount of TCP loading and observed characteristic peaks of TCP during MO degradation, are attributed to be the excess TCP used, in the photosensitization step. After several attempts, optimum weight ratio of BVG to TCP was found to be 20–1, in ethanol.

3 Results and discussion

3.1 Characterization

The XRD patterns of the prepared BiVO_4 , BVG, and BVG-P samples are shown in Fig. 1a. All diffraction peaks of the pure BiVO_4 crystals can be indexed to a monoclinic BiVO_4 cell with lattice parameters of $a = 5.195$, $b = 11.701$, $c = 5.092$ Å, $\alpha = 90^\circ$, $\beta = 90.38^\circ$, and $\gamma = 90^\circ$. According to JCPDS card number 14-0688, the peaks at 2θ values of 18,

Fig. 1 **a** XRD patterns, **b** DRS analysis of the prepared samples, **c** EDX analysis of BVG, **d** EDX analysis of BVG-P, **e** IR spectra of the prepared samples

28, 30, 34, 35, 39, 42, 46, 47, 50, 53, 58, 59 can be indexed to (011), (121), (040), (200), (002), (211), (051), (240), (042), (202), (161), (321), and (123) crystal planes, respectively [29].

The XRD patterns of the prepared BVG are shown in pattern b in Fig. 1a. The characteristic peak of graphene is at $2\theta \approx 25^\circ$ [25], which shows up as a broad peak in BVG. Sharp peaks of BiVO_4 , suggest a high degree of crystallinity and the presence of two sets of XRD peaks of monoclinic BiVO_4 and graphene, indicates that both two components exist in the prepared composites and BVG is formed with a high purity.

No obvious changes are observed in the XRD pattern of the BVG-P photocatalyst relative to BVG nanocomposite. This fact is in agreement with our previous results [30]. As can be seen in the SEM images of the prepared BVG-P, the morphology of the BVG nanocomposite is changed after the photosensitization with porphyrin molecules. Porphyrin molecules cover the BVG surface. Therefore, the disappearing of graphene oxide peak at $2\theta = 25^\circ$ in the XRD pattern of BVG-P can be assigned to this fact.

The DRS analysis of the prepared samples is shown in Fig. 1b. The photonic property of the photocatalyst is a parameter affecting its photocatalytic activity. The band edge of BiVO_4 is at ~ 525 nm, also showing a strong absorption due to the inter-band transition below 520 nm in the DRS spectrum of the prepared BiVO_4 . The band gap energy of a photocatalyst is a very important factor in determining the photocatalytic performance and it can be calculated by the following Tauc equation.

$$\alpha h\nu = (h\nu - E_g)^n \quad (1)$$

where $h\nu$ is the photon energy, E_g is the optical band gap energy, α is the measured absorption coefficient, and n is constant. For BiVO_4 as direct band gap, the value of n equals 2. The E_g value can be estimated by extrapolating the straight portion of $(\alpha h\nu)^{1/2} - (h\nu)$ plot to the $\alpha = 0$ point. Based DRS analysis the band gap of BiVO_4 has been calculated 2.47 eV. Our obtained value is in good agreement with previous reports [31, 32]. With regard to the BiVO_4 band gap and the photocatalytic results, this compound shows a moderate activity under visible light irradiation. In addition, low photocatalytic activity is shown for BiVO_4 due to the relatively narrow band gap, which correlates to an increase in the electron–hole recombination after they are formed photocatalytically. With its high charge mobility, graphene can minimize the electron–hole recombination and increase the photocatalytic activity. Based on our earlier studies, the potential of graphene in minimizing the electron–hole recombination is now investigated [33].

The presence of graphene with black color darkens the color of the prepared samples. So, the color of the

prepared samples changes from yellowish white of BiVO_4 to BVG in gray color. Due to the black color of graphene, the increase of the graphene concentration, the color of the prepared samples darkens and as can be seen in Fig. 1b consequently the absorbance of these compounds has been increased.

Porphyrin is a strong light harvesting agent and has been widely investigated in dye sensitized solar cells [28]. The sharp and strong absorption peak of porphyrin (soret band) is at ~ 400 nm. Four weak bands of porphyrin (Q bands) are in the range of 400–800 nm in the UV–Vis spectrum of porphyrin. These peaks can easily be seen in the UV–Vis spectrum of porphyrin compounds in DMF as well as EtOH solution. While, the soret and Q bands of TCPP are not obviously seen in the DRS spectrum of BVG-P photocatalyst. This fact can be attributed to the very low concentration of porphyrin on the surface of BVG-P as well as covering the effect of porphyrin with the black color of graphene. Similar results were determined in our previous articles which the presence of dark and black compounds obscures the peaks of porphyrin molecules in the DRS analysis. While, as can be seen in Fig. 2b with regard to the high absorbance of porphyrin in light harvesting, the absorbance of BVG-P compound is higher than BVG compound. In addition, the adsorption of TCPP on the BiVO_4 surface induces a broad absorption at $\lambda < 1000$ nm. This higher absorbance of BVG-P increases the photocatalytic activity of photosensitized BVG compound with porphyrin.

EDX analysis of the prepared BVG and BVG-P is shown in Fig. 1c and d. All elements of these compounds are seen in the EDX analysis of these two prepared samples. No other impurities are observed in this analysis, indicative of a clean synthetic method. The presence of nitrogen as well as higher concentrations of carbon and oxygen in the BVG-P sample relative to the BVG compound is another evidence for the existence of porphyrin in the BVG-P photocatalyst.

IR analysis of the prepared samples is shown in Fig. 1e. In the IR spectrum of BiVO_4 , a weak absorption at 1650 cm^{-1} is related to the deformation vibration of adsorbed water. Furthermore, a strong and broad peak at 1261 cm^{-1} can be assigned to the lattice vibration of BiVO_4 [34]. In the IR spectrum of TCPP, the COO peak is observed at 1687 cm^{-1} [35]. With attaching TCPP on the surface of BiVO_4 through esteric bond as well as with regard to the low concentration of porphyrin on the BiVO_4 surface, the intensity of the COO peak in the BVG-P sample is low and cannot be simply observed. Although, a weak peak at 1650 cm^{-1} can be assigned to the COO group of BVG-P. In a report by Tada et al, the peaks at 1580 cm^{-1} and 1430 cm^{-1} can be related to the asymmetric and symmetric stretching vibrations of the COO [34]. In the IR spectrum of our prepared BVG-P, Similar weak peaks are also observed in these ranges.

Fig. 2 SEM images of the prepared **a** BiVO_4 , **b** and **c** BVG, **d**, **e**, and **f** BVG-P compounds

These peaks are not observed in the IR spectrum of BiVO_4 as well as BVG. So, the IR analysis also is suggestive porphyrin is attached to the BiVO_4 surface in BVG-P.

The morphology and microstructure of the prepared samples were studied by scanning electron microscopy (SEM). The SEM image of the prepared BiVO_4 is shown in Fig. 2a and as can be seen, the prepared pure BiVO_4 crystals exhibit a plate-like morphology with a thickness of about 200–300 nm. In addition, the surfaces of BiVO_4 crystals are smooth.

As can be seen in the Fig. 2b, the sheet-like morphology of the BVG sample is obvious in the SEM image of the prepared BVG 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. Furthermore, in the BVG compound due to the presence of graphene sheets the size of BVG plates is reduced. In the BVG compound, the BiVO_4 plates are decorated on the graphene sheets separately and the aggregation of BiVO_4 plates is decreased. Thus, the size of the plates reduces.

The very interesting images of the BVG-P compound are shown in Fig. 2d–e. As can be seen in these figures, the BVG compound is arranged in pineapple-like slabs. It is notable that until now in our works, the photosensitization of porphyrin has no effect on the morphology of metal oxide. In the previous works, the smaller particles were formed in the presence of porphyrin in the prepared samples. While, in the prepared BVG-P compound, the photosensitization with TCPP causes to form the compound with the interesting pineapple slab-like morphology.

The formation mechanism of this morphology can be described as follows. In the BVG-P compound, The BiVO_4 plates are decorated on the both faces of the graphene sheets. It is determined that hydroxyl groups exist on the metal oxide surfaces. In addition, The TCCP molecule has

four carboxyl groups. Therefore, TCCP molecule can be attached on the BiVO_4 surface which is decorated on two both faces of graphene sheets. This arrangement happens cyclic to form the three-dimensional structure of BVG-P compound. The schematic representation of the formation 3D structure of the BiVO_4 -P compound is shown in scheme 1.

3.2 Photocatalytic performance of the prepared samples

The photocatalytic activity of the prepared samples was measured at 25 °C to degrade a 10 mg/L MO aqueous solution under visible light irradiation of the white LED lamp. Photocatalytic comparative investigation of the

Scheme 1 The formation process of the 3D structure of BVG-P

Fig. 3 **a** Photocatalytic comparative investigation of the prepared samples in degradation of MO 910 ppm, **b** UV–Vis spectrum changes of MO by the prepared BVG-P over time

prepared samples is shown in Fig. 3a. The photocatalytic activity improvement of the prepared BiVO_4 is the purpose of this study. As can be seen in Fig. 3a, the prepared BiVO_4 plates can remove 69% of MO dye pollutant in 240 min under the visible light irradiation. To improve the photocatalytic activity, the prepared BiVO_4 was mixed with graphene. Photocatalytic investigations determined that the optimum content of graphene is 0.5% in the BVG nanocomposite.

The prepared BVG nanocomposite was photosensitized with TCPP to improve the visible light photocatalytic activity. Figure 3b shows the absorption spectral changes of MO in the photodegradation process over the BVG-P nanophotocatalyst. As shown in Fig. 3b, the main absorption peak of the MO dye pollutant decreases within the exposure time and completely disappears after 180 min. This indicates the total decomposition of MO dye pollutant over the BVG-P nanophotocatalyst. The results of the photocatalytic degradation determined that at 30 min of the photocatalysis process the photocatalytic activity of the prepared BVG nanocomposite enhances 3.5 times after the photosensitization with porphyrin. The BVG-P compound shows 78% efficiency in the photodegradation process at 30 min of visible light irradiation. This high photocatalytic activity at the first time of irradiation shows the high ability of porphyrin to absorb the visible light and improvement of the photocatalytic activity of the prepared compound. The comparative investigation determines that the prepared BVG-P photocatalyst shows the better kinetic photodegradation rather than the prepared BVG nanocomposite. This compound has destructed 78%, 87%, and 97% of the MO dye pollutant at 30 min, 60 min, and 150 min respectively.

3.3 Photocatalytic activity description of BVG-P

Photoinduced electrons and holes play the main role in the photocatalysis process. It is well known that the photodegradation efficiency is strongly dependent on the electron–hole pairs produced by light irradiation on

photocatalysts [36]. The electron–hole recombination has an important effect on the photocatalysis process [37]. In this process, electron and hole are produced at the surface of the photocatalyst after light irradiation. The photoinduced electron and hole have two reaction pathways, some of them migrates to the surface of the photocatalyst and then can be trapped generally by O_2 from air, and surface hydroxyls to produce radical species which then react with the adsorbed reactants (here MO). While, some of them comes back to the valence band of the photocatalyst and recombine with the residual holes [38].

In our study the recombination in BiVO_4 photocatalysis process decreases the efficiency of the reaction. The prepared BiVO_4 plates removed 69% of MO dye pollutant after 4 h of visible light irradiation. DRS analysis determines that the band gap of the prepared BiVO_4 is 2.47 eV. Therefore, the photocatalytic efficiency of the prepared BiVO_4 with relatively narrow band gap, is negatively affected by electron–hole recombination processes. Two methods were used in this study to increase the photoactivity of the prepared BiVO_4 under visible light irradiation. In step one, we used graphene and in step 2 the prepared sample was photosensitized with porphyrin.

3.3.1 The effect of graphene

To decrease the electron–hole recombination and subsequently enhance the photocatalytic activity, the prepared BiVO_4 was mixed with graphene. To determine the optimum content of graphene, the prepared BiVO_4 was mixed with 0.2, 0.5, and 1 weight percentage of graphene. Photocatalysis experiments show that the BVG nanocomposite with 0.5% of graphene has the highest photoactivity under the visible light irradiation. 0.5% of graphene has the highest ability to decrease the recombination and subsequently enhance the photoactivity of the prepared BVG nanocomposite. More content of graphene covers the BiVO_4 surface and prevents the light from getting into the semiconductor. Thus, with increasing the content of graphene, the active sites of BiVO_4 are covered. Therefore,

0.5% of graphene was selected the optimum content in the preparation of the BVG nanocomposite.

3.3.2 The effect of porphyrin

Visible light driven photocatalyst is the main challenge in the photocatalysis process. Porphyrin is a well-known compound in dye sensitized solar cells. This compound can absorb a wide range of light. It is known as a light harvesting agent. To increase the visible light photocatalytic activity of the prepared BVG nanocomposite, the photosensitization process was done with TCPP.

In the first step, the concentration of TCPP was investigated in the photosensitization process. For this purpose, the ratio of 1:20, 1:10, and 3:10 contents of TCPP to BVG were investigated in the photosensitization process. The results of these photocatalytic investigations are shown in Fig. 4. The photodegradation of MO dye pollutant over the photosensitized BVG nanocomposite shows that in high concentration of TCPP, the low photocatalytic activity is obtained. Due to the aggregation of porphyrin molecules on the BiVO_4 surface, the efficiency of porphyrin activity in light harvesting and electron transfer decreases in the photocatalysis process. Furthermore, in high concentration of TCPP, some of the porphyrin molecules weakly bonds on the BVG surface and releases during the photocatalysis process. An optimum photocatalytic activity is achieved over the TCPP photosensitized BVG with 1:20 ratio of porphyrin to the BVG nanocomposite. In this compound the porphyrin molecules decorate on the BiVO_4 surface separately and little aggregation of TCPP molecules occurs.

In the proposed photocatalytic degradation mechanism of MO by BVG-P (Scheme 2), the electron-hole pairs are generated on the BiVO_4 surface under visible-light irradiation. Enhancement in photocatalytic activity under

light irradiation depends on an efficient separation of photogenerated electrons and holes. In this case, graphene in BVG, effectively reduces the recombination of electrons and holes. During the photocatalytic reactions, electrons from the valence band of BiVO_4 are excited to the conduction band under visible light irradiation, then the photo-generated electrons migrate to graphene. Graphene sheets with high charge mobility transfer the photoinduced electrons and holes in the opposite direction. Afterward, for more efficiency of toward visible light, BiVO_4 -graphene nanocomposite was photosensitized with porphyrin. In BVG-P, the porphyrin molecules are excited under visible light irradiation. The excited electrons of porphyrin transfer from TCPP to BVG.

As illustrated in the SEM image of BVG-P photocatalyst, the resulted 3D morphology after photosensitization of the BVG nanocomposite with TCPP can trap dye pollutant molecules inside BVG-P channels and more pollutant molecules will exist in the vicinity of the photocatalyst. Thus, it can be described that the high photocatalytic activity of the BVG-P compound at the beginning of photodegradation relates to the proper morphology of BVG-P. After 60 min of light irradiation, 87% of MO is destructed by BVG-P. After this time, the efficiency of photodegradation decrease. Scheme 3, summarizes the performance results of BVG-P. The strong oxidizing condition created by the presence of highly reactive radical species that are responsible for the degradation of MO, is thought to be able to oxidize TCPP as well, during time. In an ongoing study, this issue is addressed by decreasing the oxidation potential of TCPP by metalating it and installing electron-withdrawing substituents.

3.3.3 Comparison study

To get a better picture of the efficiency of our prepared photocatalyst, BVG-P is compared with other BiVO_4 based reported samples and the results are summarized in Table 1. Tayade and coworkers have made $\text{BiVO}_4/\text{GeO}_2$ to destruct Rhodamine B (RhB) dye pollutant under visible light irradiation. The photodegradation process with 92.2% efficiency was carried out over the prepared

Fig. 4 Concentration porphyrin effect on the photocatalytic activity of the prepared BVG-P

Scheme 2 Proposed mechanism of the photocatalytic degradation of MO by BVG-P

Scheme 3 Schematic representation of the photodegradation process of MO trapped between graphene sheets over the prepared BVG-P photocatalyst

Table 1 Photocatalytic activity of other prepared compounds with BiVO₄

Photocatalyst	Pollutant	Reaction time	Efficiency (%)	Light source	References
GeO ₂ /m-BiVO ₄	RhB ¹	4 h	92.2	Sunlight	[39]
BiVO ₄ /WO ₃	2-chlorophenol	180 min	92.1	Xe lamp 150 W	[40]
BiOCl/BiVO ₄	RhB	4 h	96	Visible light	[41]
BiVO ₄ -ZnO	Wastewater	~6 h	64	Sunlight	[42]
BiVO ₄ -GO-PTFE	MB ²	180 min	90	Xe lamp 500 W	[43]
BiVO ₄ /Mn ₃ O ₄	MB	180 min	100	LED lamp 5 W	[7]
BiOI/BiVO ₄	MB	250 min	89	Xe lamp 500 W	[44]
BiVO ₄ /TiO ₂	MB	6 h	92.5	Halogen lamp 500 W	[45]
BiPO ₄ /BiVO ₄	MB	4 h	96	75 W metal halide	[46]

¹Rhodamine B

²Methylene blue

photocatalyst in 4 h under sunlight irradiation [39]. In the work of Suganthi and coworkers, 92.1% of 2-chlorophenol was destroyed over the BiVO₄/WO₃ sample at 180 min under UV light irradiation of 150 W Xe lamp [40]. The photocatalytic activity of the BiOCl/BiVO₄ microspheres was investigated in the work of Zheng et al. [41]. The prepared photocatalyst can destroy 96% of the RhB dye pollutant using visible light. [41] Heterostructured BiVO₄-ZnO mixed oxide catalyst was synthesized with Raghava Rao et al. [42]. The photodegradation results determined that 64% of pollutants in wastewater were destroyed at nearly 6 h under solar light irradiation [42]. In another investigation 90% of methylene blue dye pollutant was destroyed over BiVO₄-graphene oxide-PTFE nanocomposite in 180 min

[43]. The 500 W Xe lamp was used as the visible light irradiation in this work. In these reported examples, the electron-hole recombination in BiVO₄ is decreased upon forming a composite with other compounds. Comparison with these works determines that the recombination of BiVO₄ has decreased effectively with the composition of graphene with high charge mobility. The prepared BVG-P in our work can destroy 99.04% of MO. The 40 W white LED lamp was used as the low power of visible light irradiation. Therefore, porphyrin photosensitizer acts as a strong, visible light harvesting agent and efficiently increased the photocatalytic activity of the prepared BiVO₄-graphene under visible light illumination.

Fig. 5 **a** Photocatalytic activity of the prepared BVG-P in the presence of different scavengers, **b** reusability investigation of the prepared BVG-P

3.4 Determination of the active species in the photocatalysis process

To determine the active species in the photocatalysis process of the BVG-P sample, hydroxyl radicals $OH^\cdot$, superoxide radicals $O_2^{\cdot-}$ and holes (h^+) were examined by adding t-BuOH (1 mmol) (as a scavenger of $OH^\cdot$), N_2 gas (as the control condition for the role of O_2) and ammonium oxalate (2 mmol) (as a scavenger of h^+) respectively at room temperature. The results show in Fig. 5a.

As can be seen in this figure, the photodegradation of MO is effectively reduced by purging of N_2 gas in the photocatalytic reactor. Thus, the photogenerated $O_2^{\cdot-}$ species have the main role in the photocatalysis process of the BVG-P sample. In the absence of O_2 the reaction does not happen such as in the case when the reaction is done under N_2 atmosphere and O_2 free conditions. The role of porphyrin in the generation of singlet oxygen have been widely investigated [47]. Porphyrin molecules are excited upon the light irradiation. The oxygen molecules are converted to the singlet oxygen by the photogenerated electrons. The generated singlet oxygen is the reactive species that reacts with MO and oxidizes it. However, the photodegradation efficiency of MO is decreased by the addition of t-BuOH as well as ammonium oxalate. So, the photogenerated $OH^\cdot$ radicals and holes are also play an important role in the photocatalysis process.

3.5 Stability and reusability of the prepared BVG-P photocatalyst

The stability and reusability of the catalyst is an important parameter in the industrial applications.

Therefore, in order to evaluate this, BVG-P was reused in 4 successive cycles of degradation experiment under the same experimental condition (50 mL MO solution, 25 °C, irradiated by 40 W LED lamp for 180 min). For this test 0.05 g of the BVG-P was introduced into the reaction and at the final time of the photodegradation, the

photocatalyst was collected as well as dried and used for the second run of the photocatalysis process. The results of the stability test are shown in Fig. 5b. As can be seen in this figure, no obvious change in the photocatalytic efficiency is observed in the first two cycles of reaction. The decline in the photocatalytic efficiency after the second cycle is attributed to strongly oxidizing conditions being responsible for degrading MO, to also oxidize the porphyrin framework of the composite. Preliminary data suggest that this issue can be addressed by tuning the oxidation potential of porphyrin by metalation or by electron-withdrawing substituents. This test also determines that porphyrin has the important role in the improving of visible light photocatalytic activity of BVG-P sample.

4 Conclusions

In this work, the nanocomposites of $BiVO_4$ and graphene were prepared with different contents of graphene. The photodegradation results determined that the BVG nanocomposite with 0.5% of graphene show higher photocatalytic activity among the prepared nanocomposites. The very interesting pineapple slabs like morphology was obtained through photosensitization of the BVG nanocomposite with TCPP. It is proposed that in this morphology, dye pollutant molecules trap inside the channel of the BVG-P compound and more pollutant molecules will exist in the vicinity of the photocatalyst. An optimum photocatalytic activity is achieved over the TCPP photosensitized BVG with 1:20 ratio of porphyrin to the BVG nanocomposite. The BVG-P compound shows 78% efficiency in photodegradation process at 30 min of visible light irradiation. The effect of graphene in decreasing electron-hole recombination and porphyrin in absorption of visible light discussed in also studied. The radical scavenger tests determined that all the $O_2^{\cdot-}$, $OH^\cdot$ species, and photoinduced hole are involved in the photocatalysis process of the prepared

BVG-P compound. While, O_2^- Plays the more important role in this process.

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Compliance with ethical standards

Conflict of interest There are no conflicts to declare.

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