

Review

Advances in Synthesis and Applications of Bismuth Vanadate-Based Structures

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Abstract

In recent years, researchers have made great efforts to develop effective semiconductor photocatalysts to harness the visible spectrum of sunlight in photocatalytic applications. Bismuth vanadate, BiVO₄, has emerged as one of the most promising candidates for photocatalytic applications among the few non-titania-based visible-light-driven semiconductor photocatalysts. BiVO₄-based structures are intensively studied due to their exceptional ionic conductivity, photocatalytic behavior under ultra-violet and visible light, dielectric properties, ferroelastic and paraelastic phase transitions, and strong pigmentation. BiVO₄ occurs in nature in three crystalline structures: orthorhombic pucherite, tetragonal dreyerite (tz), and monoclinic clinobisvanite (ms). All three crystal structures of BiVO₄ are n-type semiconductors with corresponding energy gap values of 2.34, 2.40, and 2.90 eV, respectively. Different methods of synthesis have been reported for the preparation of BiVO₄ structures of varying morphologies and sizes. The morphology of BiVO₄ is strongly influenced by the preparation method and reaction parameters. A comprehensive systematic study of developments, preparation methods, structure, properties, and advances in different applications over the past decades in research on BiVO₄-based structures will be described. Finally, the current challenges and future outlook of BiVO₄-based structures will be highlighted, in the hope of contributing to guidelines for future applications.

Keywords: bismuth vanadate; tetragonal structure; monoclinic structure; photocatalytic properties; degradation organic pollutants; water splitting; photoanode; photoelectrochemical (PEC) sensor; antibacterial properties; food industry



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1. Introduction

Water pollution is one of the most serious of all environmental problems, with critical effects on human life. Photocatalytic degradation technology, including advanced oxidation processes (AOPs), has become increasingly more useful, if not fully necessary, in the past few decades due to the larger presence of a wide range of organic and inorganic contaminants. Obtaining photocatalysts with ideal performances is the core problem for photocatalysis [1,2].

In recent decades, immense research attention has been focused on solving the pollution problem and developing different kinds of semiconductor photocatalysts. A series of photocatalysts have been designed for this purpose. Since the wide use of pure titania

(TiO₂) photocatalyst is limited to ultra-violet (UV)-driven processes and applications, alternative materials, including doped titania and composites, are being extensively explored. In particular, owing to their unique properties, Bi-based semiconductor photocatalytic materials have been widely studied [2]. Bismuth vanadate (BiVO₄) shows great photocatalytic features that extend its use beyond the UV region due to its suitable band gap of 2.4 eV and favorable band edge alignment to water splitting. BiVO₄ shows interesting physicochemical and dielectric properties, ferroelasticity, semiconductivity, and pigmentation. BiVO₄ is polymorphous and occurs in three forms, which can be prepared synthetically: a scheelite-type structure with monoclinic (ms-) and tetragonal (ts-) systems, and a zircon-type structure with a tetragonal system (tz-). All three crystalline phases, ts-BiVO₄, ms-BiVO₄ and tz-BiVO₄, are n-type semiconductors with band gap energies of 2.34, 2.40, and 2.90 eV, respectively. A fourth form, i.e., an orthorhombic structure of BiVO₄, only occurs naturally as the mineral pucherite. As one of the promising non-titania visible-light-driven photocatalysts, ms-BiVO₄ is studied intensively, and many ways to prepare ms-BiVO₄ micro- and nanoparticles of varying morphologies and sizes have been tested. Also, due to its yellow color, non-toxic ms-BiVO₄ is a good commercially available substitute to toxic cadmium- and lead-based yellow pigments [3,4].

Following the work of Kudo's group in 1998 on the photocatalytic evolution of O₂ under visible light irradiation of BiVO₄ in aqueous AgNO₃ solution [5–7], considerable research efforts have been devoted to BiVO₄-based material. This material is an excellent candidate for use in photocatalytic water splitting and the photocatalytic degradation of air/water pollutants [8,9]. ms-BiVO₄ is known to exhibit excellent photocatalytic activity under visible light; on the other hand, pure tz-BiVO₄ has been studied to a much lesser extent as a photocatalyst [10–12].

In order to improve the photocatalytic performance of BiVO₄, promoting the separation and transfer of photogenerated carriers, namely, the photoinduced electron (e[−]) and hole (h⁺) pairs, is necessary [4,13]. There are a lot of BiVO₄-based heterojunction photocatalysts, including n-BiVO₄@p-M [14], CaFe₂O₄/BiVO₄ [15], TiO₂/BiVO₄ [16,17], rGO/BiVO₄ [18], Bi₂WO₆/BiVO₄ [19], Co₃O₄/BiVO₄ [20], BiVO₄/Bi₄V₂O₁₁ [21], Ag₃PO₄/BiVO₄ [22], Cu₃Mo₂O₉/BiVO₄ [23], BiVO₄/CdS [24], Bi₂S₃/BiVO₄/MgIn₂S₄ [25], and 2D Zn-MOF/BiVO₄ [26], which have been developed for the photocatalytic decomposition of water, degradation of organic pollutants, and reduction of CO₂ and heavy metal ions [27–29]. Enhanced photocatalytic performance has been reported for numerous doped BiVO₄ materials with a zircon-type structure. Bi³⁺-based compounds can be easily doped with rare ions (RE³⁺) due to the equal valence and similar ionic radius. This means that RE³⁺ ions could be regarded as active co-catalysts and dopants to enhance the photocatalytic activity of BiVO₄ [30–32]. Also, other dopants like Cu²⁺, Yb³⁺, Er³⁺, Nd³⁺, and Sm³⁺ ions can induce modifications of BiVO₄ shape, increase its active area, and drastically change its optical properties, while transition metals molybdenum Mo⁶⁺ and tungsten W⁶⁺ can improve the electrical characteristics, electron mobility, and electrical conductivity of BiVO₄ [33–38].

This review will be focused on the state of the art of the basic and applied research on BiVO₄-based structures. A comprehensive systematic study of developments, preparation methods, structure, properties and advances in everyday applications over the past decades in research on BiVO₄-based structures will be described.

2. Discussion

2.1. Advances in Synthesis of BiVO₄-Based Structures

Different methods of synthesis have been reported for the preparation of monoclinic ms-BiVO₄ or tz-BiVO₄ with various morphologies and sizes. Several approaches have been used: co-precipitation and micro-emulsion [11,39–46], hydrothermal synthesis with and

without the use of surfactant or template [47–54], rapid microwave-assisted processes and microwave-assisted hydrothermal methods [55–62], and solvothermal approaches [63–69]. Using a precipitation method, BiVO_4 can be obtained from an aqueous solution of NH_4VO_3 and an aqueous nitric acid solution of $\text{Bi}(\text{NO}_3)_3$ [42,56,70–72] or from an aqueous nitric acid solution of Bi_2O_3 and V_2O_5 [12,73]. By using a microwave-assisted or hydrothermal technique, either an aqueous NaVO_3 or NH_4VO_3 solution was mixed with nitric acid (HNO_3) and $\text{Bi}(\text{NO}_3)_3$ solution, or mixture of the Bi_2O_3 and V_2O_5 in a molar ratio in HNO_3 [60,74–78].

Several specialized methods have also been developed for the synthesis of BiVO_4 . These include: (i) a reaction involving layered potassium vanadate powders (KV_3O_8 and $\text{K}_3\text{V}_5\text{O}_{14}$) and $\text{Bi}(\text{NO}_3)_3$ in aqueous solution, using a controlled vanadium-to-bismuth ratio [79]; (ii) a high-temperature colloidal synthesis in which $\text{Bi}(\text{NO}_3)_3$, NH_4VO_3 , and polyethylene glycol (PEG) are dissolved in water [80]; and (iii) a low-temperature molten salt method employing a LiNO_3 – NaNO_3 eutectic mixture (heated to 200 °C) as the solvent and a BiVO_4 precursor, obtained as a precipitate from $\text{Bi}(\text{NO}_3)_3$ and NH_4VO_3 solutions, as the solute [81]. Structural phase transition in BiVO_4 (from monoclinic to tetragonal) can occur under high pressure [82,83].

$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used in most syntheses of BiVO_4 as a bismuth precursor owing to its wide availability and cheapness. However, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ readily hydrolyzes into basic salts, $\text{BiO}(\text{NO}_3)$ and $\text{Bi}(\text{OH})_2\text{NO}_3$, and other nitrates with numerous complicated compositions [84,85]. Recently, a novel and non-conventional synthesis method was attempted through a straightforward room-temperature non aqueous preparation method for producing nanocrystalline tz- BiVO_4 : NH_4VO_3 and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ were employed as precursors, with ethylene glycol (EG) serving as both the solvent and reaction medium for precipitation. Additionally, EG functions as a capping agent, limiting particle growth and preventing agglomeration [86–88].

Figure 1 schematically illustrates the formation process of the monoclinic/tetragonal BiVO_4 heterostructure (m-t BiVO_4), which involves nucleation followed by aggregation-driven growth. The phase transition from the monoclinic to the tetragonal structure is attributed to the stability of the 2-methoxyethanol (MEOH)–Bi complex formed during solvothermal treatment. In this process, Bi^{3+} ions coordinate with both the oxygen atom of the C–O–C bond and that of the O–H bond in the MEOH molecule. Notably, the relative intensity of the (200) diffraction peak, associated with the tetragonal phase, increases with prolonged thermal treatment [89].

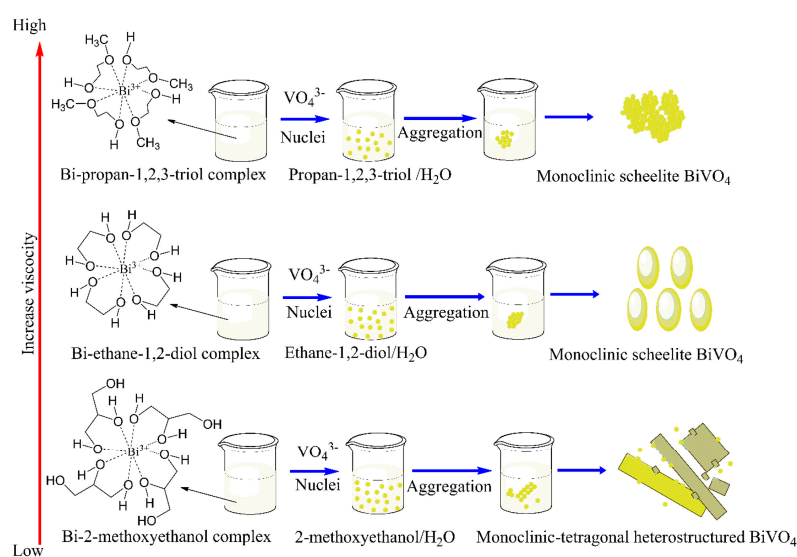


Figure 1. The formation mechanism of BiVO_4 samples prepared using mixed solvents. The image was adapted from the reference [89], with permission from Elsevier.

2.2. Advances in the Study of Morphologies and Sizes of BiVO₄-Based Structures

The morphology of BiVO₄ material has a significant impact on its photocatalytic efficiency and other applications. The final morphology is strongly influenced by the preparation method and reaction parameters, such as the concentration and pH of precursor solutions, kind of solvent, reaction temperature, duration time of preparation, molar ratio of Bi³⁺/V⁵⁺, and the addition of surfactant and different dopant ions. The morphology of BiVO₄ as a photocatalyst significantly enhances the performance of ceramic membranes in oily wastewater treatment [90]. The initial pH of the precursor solution is found to be a critical parameter in defining the phase and final morphology of BiVO₄ particles [91–95]. The BiVO₄ samples prepared by different methods of synthesis have different morphologies and sizes, such as (i) highly uniform monodisperse nanospheres of 125 nm in diameter [96]; (ii) irregular spheres (20–100 nm or few micrometers) [97,98]; (iii) hollow spheres (~700 nm) [99,100]; and (iv) nanorods (length of 300 nm) [101,102]. Other BiVO₄ particles with unusual morphologies have been realized, including the following: needle (50–400 nm), irregular dog-bone (300–600 nm) [103], butterfly (4–10 µm) [63], leaf peanut (1–10 µm), roundish aggregates (1–5 µm) [57,104,105], polyhedral (6–8 µm) [45,106] and decagonal shape rods (2–3 µm) [107], potato- and broccoli-like (150–500 nm) [108], bowknot (5 µm), and dumbbell-like (~3 µm) [109]. Additionally, there are several publications about tz-BiVO₄ spherical nanoparticles with diameters in the range of 10–40 nm and an ellipsoidal shape with a radius of about 20 nm [56,110]. Compared to larger particles or bulk material, nanostructured materials with larger surface areas showed significantly enhanced reactivity and higher photocatalytic activities for water splitting under UV light irradiation [13,111].

The field emission scanning electron microscopy (FESEM) technique was generally used to observe the morphologies of BiVO₄ samples. Figure 2a,b show the prepared BiVO₄ samples, including microspheres and dumbbell-like samples, according to the use of different molecular weights of PEG in the synthesis. The results indicated that BiVO₄ with different microstructures can be selectively synthesized by simply changing the molecular weight of PEG. Also, the morphologies of samples can be controlled through varying the pH value of the hydrothermal process to obtain spindle and wheat-like BiVO₄ samples, as shown in Figure 2c,d [109].

The scanning electron microscopy (SEM) images of the BiVO₄ samples with different morphologies obtained for various Bi³⁺/V⁵⁺ molar ratios are shown in Figure 3. When the Bi³⁺/V⁵⁺ molar ratio is 1.0, micrometer-sized dumbbells (constructed from the assembly of many nanorods) with lengths of about 4–7 µm appear (Figure 3a,b), while when the Bi³⁺/V⁵⁺ molar ratio is 0.77, the obtained samples are composed of microrods with average diameter of about 1.4 µm (Figure 3c,d). As the molar ratio is reduced to 0.67 and 0.56, BiVO₄ ellipsoids with a diameter of 1.0–1.3 µm and length of 1.5–2.0 µm, consisting of many small nanoparticles, and microspheres with an average diameter of 1.1 µm are obtained, respectively (Figure 3e,h). As the Bi³⁺/V⁵⁺ molar ratio is adjusted to 0.5, the BiVO₄ particles with cake-like morphology, constituted by many small nanoparticles, and a uniform size of about 1.1 µm, are formed (Figure 3k,l). In order to obtain detailed information on the structure and morphologies of as-synthesized samples, transmission electron microscopy (TEM) can also be performed.

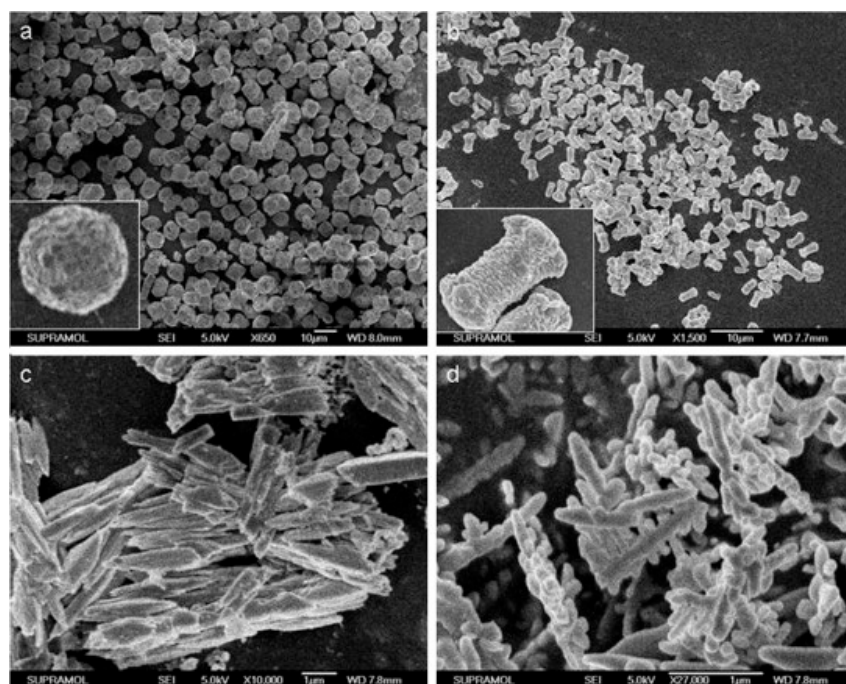


Figure 2. FESEM images of the as-prepared BiVO_4 samples: (a) spherical sample, (b) dumbbell-like sample, (c) spindle-like sample, and (d) wheat-like sample. Figure reproduced with modifications from the reference [109], with permission from Elsevier.

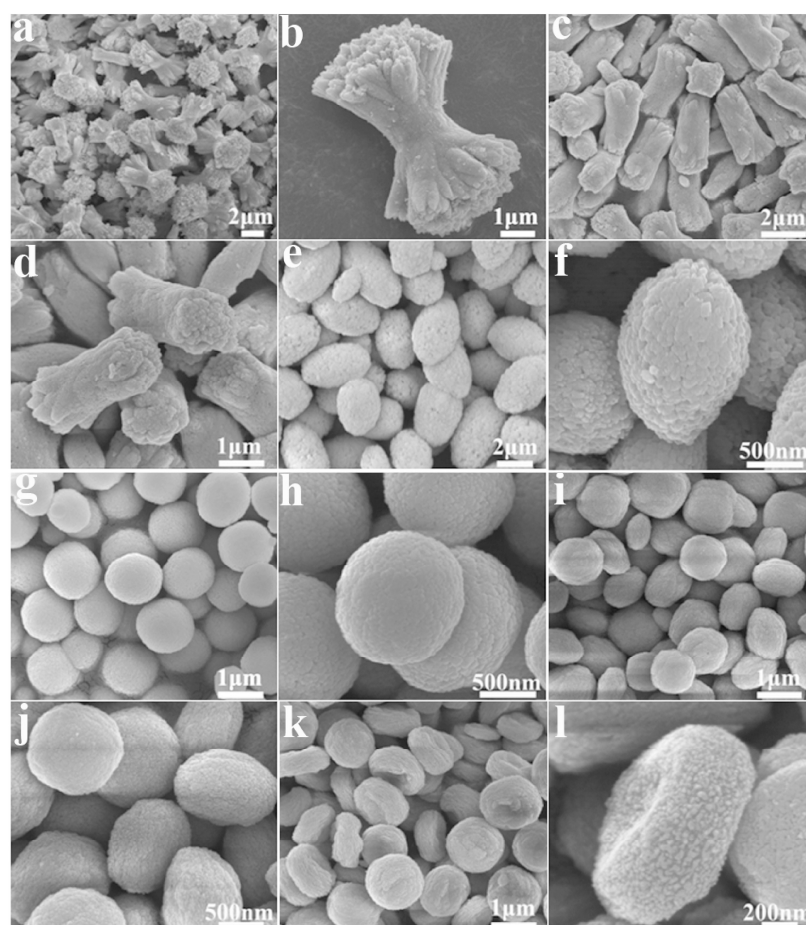


Figure 3. SEM images of BiVO_4 samples with different $\text{Bi}^{3+}/\text{V}^{5+}$ molar ratios: (a,b) 1.0, (c,d) 0.77, (e,f) 0.67, (g,h) 0.56, (i,j) 0.50, and (k,l) 0.40. The figure was adapted from the reference [112], with permission from Elsevier.

2.3. Crystal and Electronic Structure of BiVO_4

This section discusses various crystal structures and the electronic structure of BiVO_4 related to photoelectrochemical properties. As already mentioned, BiVO_4 is an n-type semiconductor and can be synthesized in three crystal phases: monoclinic-scheelite (ms), tetragonal-zircon (tz), and tetragonal-scheelite (ts), which are sketched in Figure 4. The natural structure of BiVO_4 as a mineral is pucherite with the orthorhombic crystal, and this structure cannot be obtained in the laboratory [113,114]. The scheelite structure has a tetragonal crystal system (space group: $I4_1/a$ where $a = b = 5.1470$, and $c = 11.7216$ Å) or a monoclinic crystal system (space group: $I2/a$ with $a = 5.1935$, $b = 5.0898$, $c = 11.6972$ Å, and $\beta = 90.3871^\circ$) [115], whereas the zircon-type structure consists of a tetragonal crystal system (space group: $I4_1/amd$ with $a = b = 7.303$ and $c = 6.584$ Å). In the BiVO_4 scheelite structure, each Bi atom, similar to Gd^{3+} in GdVO_4 matrix, [115] is coordinated by eight oxygen atoms from different VO_4 tetrahedral units and each V atom is coordinated by four oxygen atoms at the tetrahedral site [116], as shown in Figure 4 from the left to the right side, where Bi and V centers are coordinated along the [001] direction. At the end of the Figure there are balls of different colors that represent Bi, V and oxygen atoms. Each oxygen atom is coordinated by two Bi and one V center, forming a three-dimensional network bridging Bi and V centers together. However, the monoclinic scheelite structure shows differences, such as more distortion in the local environment of Bi and V ions, two different V-O bond lengths (1.69 and 1.76 Å), and four different Bi-O bond lengths (2.35, 2.37, 2.52 and 2.63 Å) that lead to the loss of four-fold symmetry [116]. In the tetragonal scheelite structure, all four V-O bond lengths are equal to 1.73 Å, but two different Bi-O bond lengths (2.4 and 2.47 Å) exist [116]. The observed significant distortion in the monoclinic scheelite structure enhances the local polarization, leading to better electrons and hole separation and superior photo-electrocatalytic activity compared to the tetragonal scheelite structure [117]. The local environment of Bi and V centers for the zircon-type structure is shown in Figure 4, where eight oxygen atoms coordinate Bi through six different VO_4 tetrahedral units because two VO_4 tetrahedral units provide two oxygen atoms to the Bi atom. Each V atom is coordinated by four oxygen atoms [3].

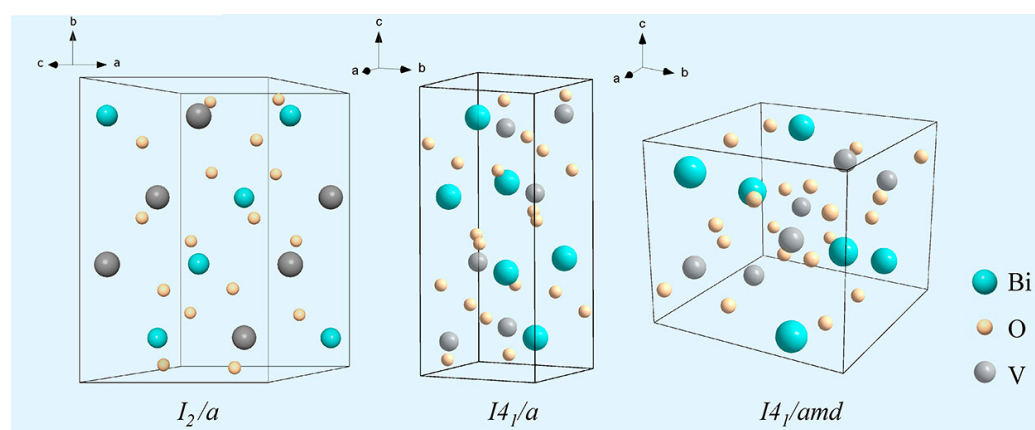


Figure 4. Graphic illustration of three crystal structures in BiVO_4 : monoclinic scheelite ($I2/a$), tetragonal scheelite ($I4_1/a$), and zircon-type tetragonal ($I4_1/amd$), respectively. The figure was adapted from the reference [82], with permission from the American Chemical Society.

The band gap energy of BiVO_4 allows it to be active in the visible region, with values of 2.4 eV for the scheelite structure and 2.9 eV for the zircon-type structure. BiVO_4 does not yet attain practical conversion efficiency. The most limiting factor for BiVO_4 conversion efficiency is the fast recombination of photogenerated electron-hole pairs [118–124]. The density functional theory (DFT) calculations indicated changes in bandgap and density of

states and showed that the smaller band gap of monoclinic bismuth vanadate, compared with the zircon type, comes from hybridization between the Bi 6s state and the O 2p states at the top of valence band [125]. The conduction band is primarily composed by V 3d states, with additional contribution of O 2p and Bi 6p orbitals [126]. The coupling of states results in an upward dispersion of the valence band and a lowering of the conduction band to a minimum, causing symmetric electron and hole masses, which facilitate a relatively efficient charge carrier separation and extraction [127]. The first-principles band structure calculations demonstrate the direct origin of the BiVO₄ band gap [86–88].

3. Advances in Applications of BiVO₄-Based Structures

3.1. Degradation of Organic Compounds: Role of BiVO₄-Based Composite Photocatalysts

This section discusses the degradation of various organic compounds in the presence of BiVO₄-based structures and composite photocatalysts. In recent years, researchers have made great efforts to develop effective semiconductor photocatalysts to harness the visible spectrum of sunlight in photocatalytic applications. A method for the degradation of toxic organic compounds/pollutants from the environment using semiconducting materials is an attractive approach. The nano-sized, ball-like structure of BiVO₄ nanoparticles can act as a good photocatalyst, sensor, and heavy metal detector. Photocatalytic efficiency was assessed through degradation studies using methylene blue (MB) dye under visible light irradiation, demonstrating an impressive 93% degradation rate [4,78,128]. In the case of the BiVO₄/graphene nanocomposite, effective degradation of methyl orange (MO) was spotted while the photocatalytic activity increased, resulting in different composites, after excitation of the BiVO₄ photocatalyst and generation of electron–hole pairs [129]. Meanwhile, the BiVO₄@MWCNTs photocatalysts were synthesized by incorporation of the synthesized BiVO₄ nanoparticles with various percentages of multi-walled carbon nanotubes (MWCNTs) and were used as probes for the photocatalytic removal of atrazine (AZ) under visible light illumination [130]. The p–n heterojunction photocatalyst prepared by decorating CuO micro-planks with spherically shaped BiVO₄ was proven to be efficient in the degradation of MB and Cr(VI) reduction under visible light irradiation. Moreover, two-dimensional (2D) TiO₂ aerogel powder decorated with BiVO₄ (TiO₂/BiVO₄) was used for the reduction of toxic Cr(VI) to Cr(III) [131,132]. Bi/BiVO₄ microstructures with a novel hollow chainlike morphology were successfully fabricated. Owing to the synergistic interaction between them, improved photocatalytic activity was observed for the photodegradation of Rhodamine B (RhB) under visible-light illumination, compared to the single photocatalytic actions of BiVO₄ and Bi [133]. The synergistic effects of oxygen vacancies and built-in electric fields in GdCrO₃/BiVO₄ and 2D/2D InVO₄/BiVO₄ heterostructures effectively enhanced their photocatalytic performance for nitrate reduction in water and improved their photoelectrochemical activity, respectively, by facilitating charge separation and suppressing recombination [134,135].

Pharmaceuticals and antibiotics have been classified as critical water pollutants. In order to find a suitable technique for removing them from contaminated water, the photoelectrocatalytic oxidation method has attracted much attention in recent years. The BiVO₄/Ag₂S p–n heterojunction fabricated by using electrodeposition and successive ionic layer adsorption on fluorine-doped tin oxide glass (FTO) or graphitic carbon nitride (g-C₃N₄) decorated with Pt@BiVO₄ have been used for the degradation of ciprofloxacin and sulfamethoxazole [136,137].

BiVO₄ has also been used in a tribocatalysis experiment utilizing magnetic stirring for the disintegration of the MB dye [138]. Figure 5 shows the UV–visible absorption peak spectra related to the degradation of MB dye in 24 h, as a function of the magnetic stirring rotation speed.

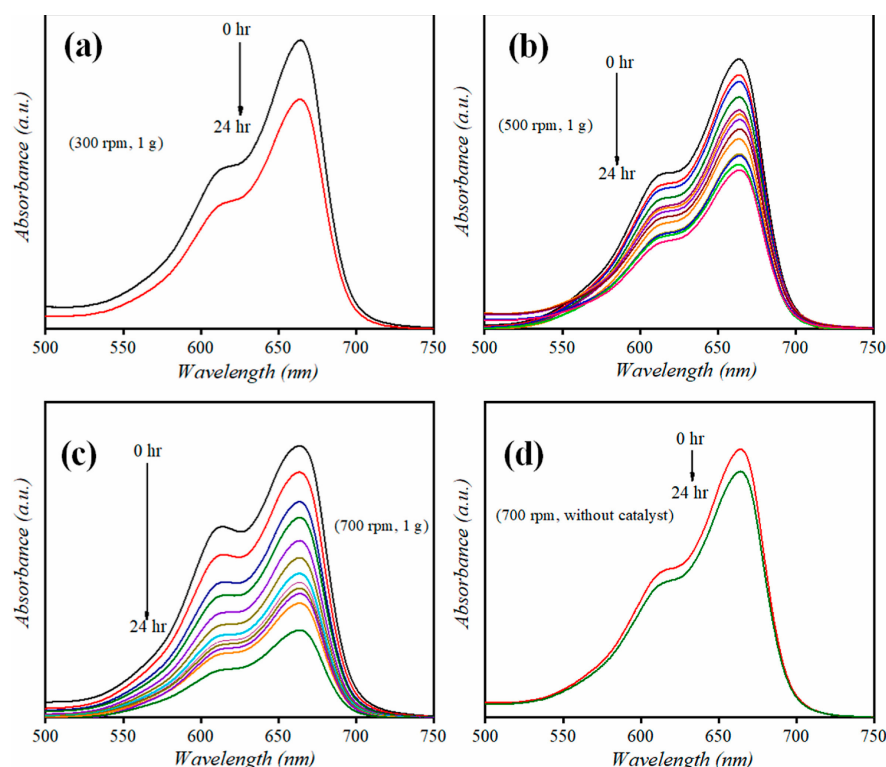


Figure 5. Absorbance spectra of MB dye in 24 h using 1 g of BiVO_4 at different rotational speeds: (a) 300 rpm, (b) 500 rpm, (c) 700 rpm, and (d) without any catalytic dose (control) at 700 rpm. The figure was adapted from the reference [138], with permission from Elsevier.

The degradation rate efficiency (D) can be calculated using Equation (1). The degradation of a dye catalyzed by BiVO_4 is analyzed using the pseudo-first-order kinetics model (Equation (2)), and the rate constant of dye degradation is calculated [139]:

$$D(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$-\ln\left(\frac{C_t}{C_0}\right) = Kt \times t \quad (2)$$

where C_0 is the initial solute concentration, C_t is the solute concentration at a certain reaction time (t), and k is the pseudo-first-order rate constant.

The sonocatalysis activity of $\text{BiVO}_4/\text{FeVO}_4$ composites was also investigated by analyzing the removal process of the drug model tetracycline (TETR). In comparison to BiVO_4 , the composites exhibited significantly enhanced sonocatalytic activity in degrading TETR due to the formation of type-II heterojunctions, which promoted effective electron-hole pair separation [140]. The improvement in photocatalytic activity is attributed to morphology, different dopant ions, light absorption efficiency, and the reduced recombination rate of the excited charge carriers. A comparison of the photocatalytic performances of BiVO_4 with different morphologies and other catalysts— TiO_2 , g- $\text{C}_3\text{N}_4/\text{TiO}_2$, $\text{V}_2\text{O}_5/\text{TiO}_2$, $\text{Nd}^{3+}\text{-TiO}_2$, Nb_2O_5 , $\text{In}_2\text{O}_3\text{-TiO}_2$, ZnO:Eu —under UV and visible light irradiation is presented in Table 1.

Table 1. Comparison of photocatalytic performances/degradation efficiencies of BiVO₄ with different morphologies and other catalysts under ultra-violet (UV) and visible (Vis) light irradiation.

Catalysts/Dose/Morphology	(Photocatalytic Parameters) Dye */Concentration/Light Source	Degradation Efficiency/Time	Ref.
BiVO ₄ /1.0 mgmL ^{−1} /peanut	MB/10 mgL ^{−1} /Xenon lamp with 35 W/m ²	40%/120 min	[141]
BiVO ₄ /1.0 mgmL ^{−1} /microtube	MO/20 mgL ^{−1} /250 W Xenon arc lamp	95%/180 min	[142]
BiVO ₄ /0.5 mgmL ^{−1} /spheres	RhB/10 ^{−5} molL ^{−1} /500 W Xenon lamp	27%/150 min	[143]
BiVO ₄ /0.5 mgmL ^{−1} /biscuits	RhB/10 ^{−5} molL ^{−1} /500 W Xenon lamp	44%/150 min	[143]
tz-BiVO ₄ /1.0 mgmL ^{−1} /spherical particles	MB/20 mgL ^{−1} /550 W Xenon lamp	20%/150 min	[144]
ms-BiVO ₄ /1.0 mgmL ^{−1} /spherical particles	MB/20 mgL ^{−1} /550 W Xenon lamp	45%/150 min	[144]
tz-BiVO ₄ /1.0 gL ^{−1} /nanoparticles	MO/5 mgL ^{−1} /300 W Osram Ultra-Vitalux lamp	100%/240 min	[86]
ms-BiVO ₄ /1.0 gL ^{−1} /nanoparticles	MO/5 mgL ^{−1} /300 W Osram Ultra-Vitalux lamp	30–35%/240 min	[86]
BiVO ₄ /1 mgmL ^{−1} /hollow nanosphere	RhB/10 ^{−5} M/500 W Xe lamp	100%/70 min	[145]
BiVO ₄ /1 mgmL ^{−1} /microtubes	MO/20 mgL ^{−1} /250 W Xe lamp	95%/180 min	[145]
TiO ₂ (Commercially)/ 0.125 mgL ^{−1} /-	BPA/10mgL ^{−1} /150 W Hmminminminaminogen lamp	9%/120 min	[146]
g-C ₃ N ₄ -TiO ₂ /0.125 mgL ^{−1} /veggie-toast-like	BPA/10mgL ^{−1} /150 W Halogen lamp	21.5%/120 min	[146]
g-C ₃ N ₄ /0.125 mgL ^{−1} /“cheese”	BPA/10mgL ^{−1} /150 W Halogen lamp	11.4%/120 min	[146]
V ₂ O ₅ /TiO ₂ coatings (anatase phase)/15 mm × 10 mm (active surface)/microdischarges	MO/8 mgL ^{−1} /Sunlight	35%/480 min	[147]
Nd ³⁺ -TiO ₂ /0.05 g/nanosphere	MB/20 mgL ^{−1} /Visible light	91.83%/120 min	[148]
Nd ³⁺ -TiO ₂ /0.05 g/nanosphere	MB/20 mgL ^{−1} /Sunlight	99.14%/80 min	[148]
Nb ₂ O ₅ /50 mg/particle clusters	RhB/1 × 10 ^{−5} M/6 UVC lamps (15 W each lamp totaling the power of 90 W-TUV Philips)	98.99%/60 min	[149]
In ₂ O ₃ -TiO ₂ /1 × 1 cm ² area/nanorods	MO/10 μM/Sunlight	86%/360 min	[150]
TiO ₂ -Degussa (P25)/1 mgmL ^{−1} /-	MB MO	35%/60 min 35%/60 min	[151]
ZnO:Eu(10%)/1 mgmL ^{−1} / nanoparticles	MO	100%/60 min	[151]

* MB: Methylene Blue; MO: Methyl Orange; RhB: Rhodamine B; BPA: bisphenol A.

3.2. Antibacterial Activity of the BiVO₄-Based Structures

BiVO₄ has also been studied as non-toxic material for potential biomedical applications due to its antibacterial activity against various pathogenic bacteria. The antibacterial activity of this material was estimated by using the pathogenic microbes *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) [152]. The photo-induced high antibacterial activity of monoclinic BiVO₄ nanoparticles has also been tested in antibacterial efficiency

and environmental remediation applications based on their photocatalytic activity targeting organic dyes and different water pollutants [153]. BiVO₄@activated carbon fiber can be used as an antibacterial agent against both *E. coli* and *S. aureus*, with enhanced recyclability [154]. Antibacterial efficacy was assessed against Gram-positive (*E. coli* and *S. aureus*) and Gram-negative (*E. coli* and *Pseudomonas aeruginosa*) bacteria using BiVO₄ and Ta-doped BiVO₄ nanoparticles at various concentrations [155]. Bacterial cultures were incubated with Ta-BiVO₄ nanoparticles under visible light illumination and in the dark for the antibacterial assays. The antibacterial activity of Ta-doped BiVO₄ nanoparticles was successfully assessed, indicating their potential as strong antibacterial agents against both Gram-positive and Gram-negative bacteria [156,157]. The antibacterial activity of BiVO₄ nanoparticles against six different bacterial strains, evaluated using the disc diffusion method, is presented in Figure 6.

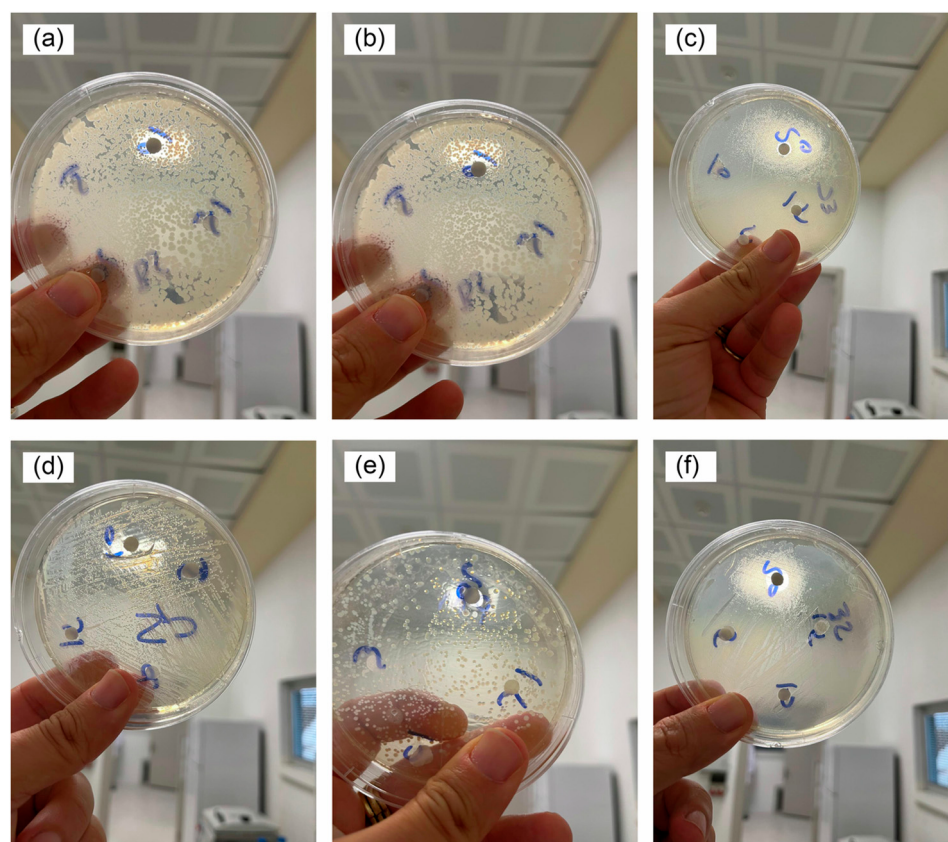


Figure 6. Antibacterial activity of BiVO₄ nanoparticles against (a) *B. subtilis*, (b) *B. cereus*, (c) *E. coli*, (d) *P. aeruginosa*, (e) *S. aureus*, and (f) *S. enteritidis*. The figure was adapted from the reference [156] under a Creative Commons 4.0 License.

N-, Cr-, and N/Cr-doped TiO₂ nanoparticles were evaluated against *Escherichia coli* under dark conditions and visible light irradiation. The results showed a clear antibacterial effect, attributed to the high degree of dispersion and enhanced electrostatic interactions [158]. Additionally, Ag-doped N-TiO₂ demonstrated antibacterial effects against selected Gram-negative bacteria commonly found in the marine environment [159]. On the other hand, antibacterial studies of Nb₂O₅-doped bioactive glasses against *E. coli* and *S. aureus* showed maximal bacterial killing in samples containing 4.0 mol% of Nb₂O₅. The results indicated that Nb₂O₅ not only enhanced bioactivity potential but also exhibited antimicrobial activity [160]. ZnO-based materials also showed antibacterial activity against different types of Gram-positive bacteria (*Bacillus manliponensis*, *Micrococcus luteus*, *Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*). The results demon-

strated that the generated O_2^- radicals played a more critical role in antibacterial activity than particle shape [161].

The antibacterial activity and the generation of reactive oxygen species (ROS) of the BiOCl/BiVO₄ heterojunction can be improved compared to BiVO₄ [162]. The ROS produced in the PDA-rGO/BiVO₄ heterojunction blocked the transmembrane transport of bacteria, as confirmed by using ROS fluorescence detection [163]. The antibacterial and UV-protection properties of the prepared CuO/BiVO₄@cotton were also studied. The CuO/BiVO₄ nanocomposite overcomes the low quantum efficiency of pure BiVO₄. The nanocomposite exhibits very good recyclability as a photocatalyst on cotton fabrics/flexible textiles, with multiple functions in addition to the degradation of pollutants from waste water [164]. The normal, inactivated tested bacterial strains with smooth surfaces are attributed to the production of ROS species such as OH and O_2^- , which easily cross the cell membrane and enter the interior of the strains [165,166].

3.3. Application of the BiVO₄-Based Structures in the Food Industry

BiVO₄ is an ideal starting material for antioxidant surveillance under visible light irradiation. BiVO₄, however, is usually doped, due to unsatisfactory charge collection and utilization in practical applications, to exploit the effects of dopants on photocatalytic behavior under visible light illumination. The substitution of Bi³⁺ or V⁵⁺ ions with other M³⁺ or M⁶⁺ metal ions leads to significant changes in physical properties, such as structural distortions of the crystal unit, formation of a new phases, and evident changes in morphological, optical, and electrical properties due to the different ionic radii of the involved ions. This proof of concept is useful for the detection of antioxidant capacity in the foodstuff industry, opening up a bright future in cosmetic and healthcare areas [167]. A label-free photoelectrochemical (PEC) sensor based on BiVO₄@GO composites was prepared for the detection of antioxidants and the antioxidant capacity of food. Large surface area and good conductivity make the BiVO₄@GO composites a unique, promising sensor for the evaluation of antioxidant capacity in food, which will help the organism obtain enough antioxidants to defend against free radicals [168], while the crystal-reconstructed BiVO₄ PEC biosensor can be applied in the fields of multi-tumor or viral biomarker detection [169]. The composition and pH of the electrolyte, applied bias, as well as surface morphology of the photoactive layer can have a significant effect on the selectivity and use of the PEC sensors [170]. The synthesized BiVO₄ PEC sensor, with a unique carnation-like morphology and high specific surface area, demonstrated high potential for Cr(VI) detection, with a wide linear range of 2–210 μ M and a very low limit of detection (LOD) of 0.01 μ M. This BiVO₃-based PEC sensor can be used, for instance, in food safety monitoring for Cr(VI) detection in peanuts, rice, soil and tap water, with satisfactory recovery rates of 90.3 to 103.0% [171].

Propyl gallate is widely used in the food industry as one of the most important additives to prevent oxidation processes. Synthesized Cu₃(PO₄)₂/BiVO₄ composites and the GCE/BiVO₄/ZrO₂@graphene electrode can be used for the determination of propyl gallate and of acetaminophen, phenylephrine hydrochloride, and cytosine, respectively, in different food products. These materials are beneficial for food quality monitoring, reduce the risk of propyl gallate overuse in food, and are recommended for potential medical applications [172,173]. A new photosensitive sensor was developed for the successful electrochemical analysis of quercetin from natural samples using an ITO/MWCNT@PC@BiVO₄ composite due to the photosensitivity and stable structure of BiVO₄, high electron permeability of MWCNT, and advantageous electron transfer [174,175]. Electrochemical and Surface-Enhanced Raman Spectroscopy (SERS) sensors based on TiO₂ or Ag-doped TiO₂ nanostructured materials have been broadly applied for detecting traces of cyper-

methrin pesticide, tartrazine, tryptamine, saccharin sodium, furazolidone, bisphenol A (BPA), histamine, and other contaminants in complex food samples [176–178]. On other hand, Pd-ZnO nanoflowers have shown to act as promising gas sensors for the detection of meat spoilage. Nb₂O₅ has been also used as a gas sensor in detecting ethanol, H₂S, H₂, NO_x, CO, and VOCs, exhibiting effective potential for applications in environmental monitoring, industrial processes, food safety, biomedicine, fuel processing, and automotive domains [179–181].

The synergic effects between g-C₃N₄ and BiVO₄ in the g-C₃N₄/BiVO₄ composites, used as a photoactive material, produced an increase in photocurrent response after the composites were fixed on the surface of the FTO electrode [182]. The illustration of the g-C₃N₄/BiVO₄ PEC sensor for tetracycline (TC) residue detection in food samples (honey) and animal products (kidney, milk, pork) is presented in Figure 7.

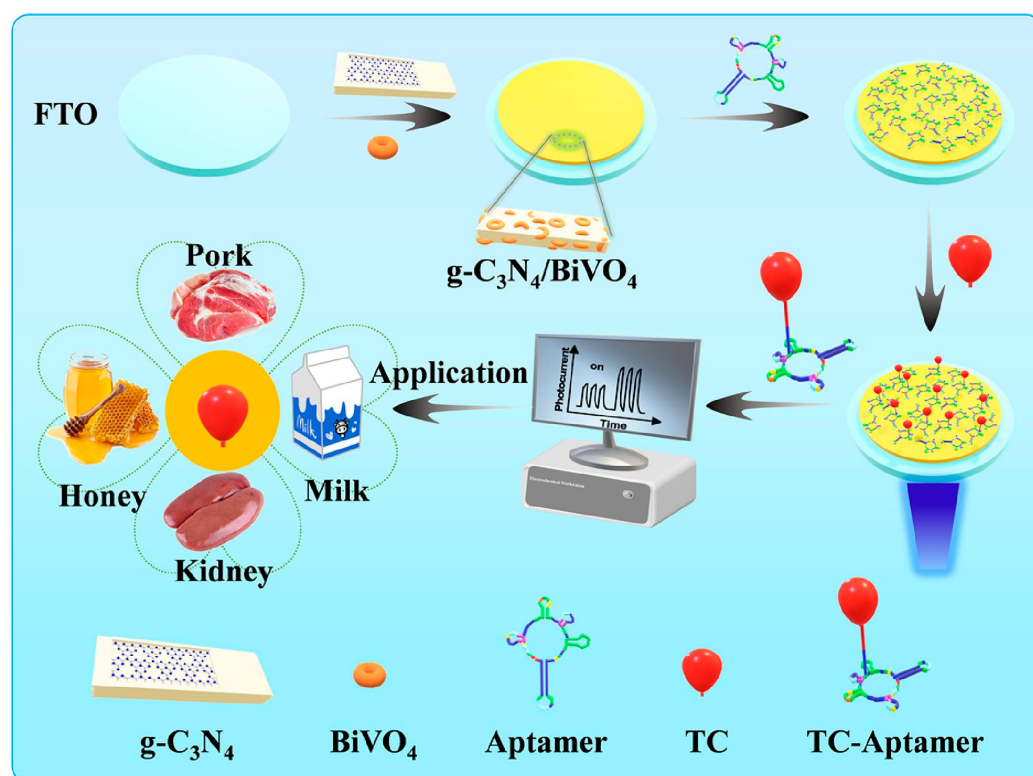


Figure 7. Schematic illustration of g-C₃N₄/BiVO₄ PEC sensor for tetracycline detection in food samples. Figure reproduced from the reference [182], with permission from Elsevier.

3.4. Applications of BiVO₄-Based Structures as Photoelectrodes in Water Splitting

In recent years, in addition to their application in environmental protection for organic pollutant degradation, antibacterial properties, and food safety monitoring, BiVO₄-based structures have also attracted attention for their multipotential applications [183]. BiVO₄-based photoelectrodes show great potential in several practical applications. Due to good visible light responsiveness and stable optoelectrical properties, BiVO₄-based structures can be widely used for efficient water splitting and hydrogen production [184,185].

To fabricate photoanodes with large areas, possessing excellent and uniform PEC activities, it is very important to include defect states of the material; thus, highly efficient BiVO₄ photoanodes containing adjustable concentrations of bismuth and oxygen vacancies, Bi_{vac} and O_{vac}, were fabricated [186]. With the aim to promote charge separation in the bulk material, a BiVO₄-based photoanode with a lattice strain was prepared by generating Bi vacancies [187]. In addition, BiVO₄ photoanodes were also used in PEC cells for the production of various chemicals, as well as for PEC water splitting [188].

Water splitting based on numerous visible-light-responsive photocatalysts is one of the most important and cost-effective approaches for the conversion of solar energy into clean and renewable hydrogen energy and the production of green H_2 on a large scale. This result can be easily achieved through a one-step excitation system using a single photocatalyst or Z-scheme strategies based on a pair of photocatalysts [189,190]. Photoelectrochemical water splitting techniques often require a corrosive electrolyte, limiting their stability and environmental sustainability; an alternative method for the clean production of hydrogen can be obtained directly from sunlight and water by photocatalytic water splitting [191].

The $BiVO_4$ material possesses several limiting parameters, including low charge mobility, high bulk recombination rates, and oxygen evolution reaction (OER) kinetics at the surface, which affects its use as a high-performance PEC photoanode for solar water splitting. Numerous strategies have been applied to improve this performance, and texture engineering has emerged as a promising approach. One approach for improving PEC efficiency is based on controlling the crystallographic orientation and exposed facets, which enhances charge transport and reduces surface recombination [192]. Following this direction in preparation, octadecahedral- $BiVO_4$ photoanodes were successfully produced with exposed {040}, {011} and high-reactivity {121} facets. It was shown that the charge separation dramatically improved, and the {121} facets showed better oxygen evolution reaction (OER) activity for triggering water oxidation than the {040} and {011} facets [193]. Other approaches for improving the PEC efficiency are based on different morphologies, doping, modification, and making different $BiVO_4$ -based composites. $BiVO_4$ nanowires, due to negative surface photovoltage signals, are suitable for the construction of membranes for solar energy conversion [194]. A suitable doping concentration of Cu in $BiVO_4$ resulted in enhanced electronic conductivity and improved charge transfer dynamics compared to un-doped $BiVO_4$ [195,196].

Multi-interfacial optimization of $BiVO_4$ -based composites to improve charge separation efficiency, due to synergistic effects within the material matrix, has emerged as a main strategy for improving PEC performance [197]. Ti_3C_2 quantum-dot-modified $BiVO_4$ photoelectrodes, $BiVO_4/Ti_3C_2$ QDs, for water-splitting H_2 production, showed improved photoelectron-hole pair separation and photocurrent density, about 2.5 times higher than that of bare $BiVO_4$ [198]. Additionally, due to the synergistic effect of CuSCN and Ni: FeOOH, the photocurrent density of the optimized $BiVO_4/CuSCN/Ni: FeOOH$ photoanode is 3.39 times higher than that of pure $BiVO_4$ [199]. A similar ratio in photocurrent density is obtained for the photoanodes $BiVO_4/Co,Fe\text{-}NTMP$ (nitrilotris-methylenephosphonic acid) and $BiVO_4$ [200]. The RGO@g- $C_3N_4/BiVO_4$ photocatalysts have dual applications in photoelectrocatalytic H_2 production and antibiotic tetracycline chloride degradation. Triple composites of g- $C_3N_4/RGO/BiVO_4$, formed by the synergistic effect between $BiVO_4$, RGO, and g- C_3N_4 , show significant photocatalytic activity compared to pure $BiVO_4$ or g- C_3N_4 [201]. Recently, an Ag/ $BiVO_4$ composite for application in an H_2O_2 fuel cell was fabricated. Compared with $BiVO_4$ nanoplates, the Ag/ $BiVO_4$ composite had a narrower band gap, enhanced visible light absorption and photocatalytic activity, and it provided a new strategy model for the efficient conversion and utilization of solar energy [202]. On the other hand, 10 cm^2 perovskite- $BiVO_4$ tandem PEC devices were fabricated with a selective $Cu_{92}In_8$ alloy catalyst which could demonstrate synthesis gas (syngas) production coupled to O_2 evolution over 36 h [203].

An example of a photocatalytic system based on $BiVO_4$ composites is presented in the scheme shown in Figure 8. The system is composed of two separate reaction parts: a hydrogen evolution cell containing halide perovskite photocatalysts ($MoSe_2$ -loaded $CH(NH_2)_2PbBr_{3-x}I_x$) and an oxygen evolution cell containing NiFe-layered double hydroxide-modified $BiVO_4$ photocatalysts mediated by the I_3^-/I^- redox shuttle [204].

Table 2. Cont.

Material BiVO ₄		
Crystal Forms/Band Gap (Eg)		Ref.
Method of synthesis	Morphology	
Co-precipitation; micro-emulsion; hydrothermal synthesis with and without surfactant or template; rapid microwave-assisted process; microwave-assisted hydrothermal method and solvothermal approach.	Ellipsoidal; highly uniform monodisperse nanospheres; irregular spheres; hollow spheres; nanorods; needles; irregular dog-bone; butterfly, leaf peanut roundish aggregates; polyhedral; decagonal shape rods; potato and broccoli-like; bowknot; dumbbell-like; spherical nanoparticles.	[11,39–69] [45,56,57,63,96–110]
Advantages/Applications	Disadvantages/Future work	
Narrow band gap; yellow color of powder; pigmentation; cost-effectiveness; ease of synthesis; photocatalytic water splitting; photocatalytic degradation of air/water pollutants; reduction in CO ₂ and heavy metal ions; antibacterial agents; antioxidant, food safety monitoring; gas sensor; PEC sensor; H ₂ production; electrodes.	Fast recombination of photogenerated electron–hole pairs; developing novel synthesis techniques; industrial-scale production; improving the charge separation efficiency	[6,15,16,27–29,31,50,60,71,77,167,168,204]

4. Conclusions

This review has provided a systematic study and a related bibliography concerning developments, preparation methods, structures, properties, applications, and recent advances of the research on BiVO₄-based structures. Compared with the limitations of pure TiO₂ in UV-range applications, BiVO₄ offers superior photocatalytic properties operating beyond the UV region. Its narrow band gap of 2.4 eV makes it particularly favorable for water splitting. In addition, BiVO₄ exhibits excellent physicochemical and dielectric properties. Moreover, due to its yellow color and non-toxic nature, monoclinic scheelite BiVO₄ represents a commercially viable alternative to toxic cadmium- and lead-based yellow pigments.

A detailed discussion was presented regarding the preparation approaches, processes, morphology, crystal and electronic structure, performance, and applications of BiVO₄-based structures. The morphology of BiVO₄ material has a significant impact on its photocatalytic efficiency. The final morphology is strongly influenced by the synthesis preparation method and reaction parameters, such as concentration and pH value of precursor solutions, kind of solvent, reaction temperature, preparation time, Bi³⁺/V⁵⁺ molar ratio, surfactant addition, and the presence of different dopant ions. The enhanced photocatalytic activity can be attributed to morphology, improved light absorption due to a lower band gap, and reduced recombination rate of excited charge carriers.

A method of degrading toxic organic compounds/pollutants in the environment using semiconducting materials constitutes a very attractive approach. Photodegradation of various organic compounds like methylene blue, Rhodamine B, and atrazine, as well as pharmaceutical species, such as ciprofloxacin and sulfamethoxazole, in the presence of BiVO₄-based photocatalysts under visible light irradiation was explained in detail. BiVO₄ has been studied as a non-toxic material with high potential for biomedical applications due to its antibacterial activity against various pathogenic bacteria microbes, e.g., *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*). Additionally, BiVO₄ has been studied as an ideal starting material for antioxidant surveillance under visible light irradiation to assess the antioxidant capacity of foodstuffs, opening up a bright future for these materials in cosmetic and healthcare applications as well. Moreover, BiVO₄ as biosensor can be applied in the fields of multi-tumor or viral biomarker detection. Due to good visible light responsiveness and stable optoelectrical properties, BiVO₄-based structures have also been studied as photoanodes for efficient water splitting and hydrogen production, as well as high-performance photoelectrochemical (PEC) sensors.

Despite its many advantages, such as a narrow band gap (2.40 eV for ms-BiVO₄), yellow color, pigmentation, cost-effectiveness, and ease of synthesis, the most dominant disadvantages of BiVO₄ are based on the fast recombination of photogenerated electron–hole pairs.

Looking into the future, research on BiVO₄-based structures should be focused on developing novel synthesis techniques for nanostructure design and for industrial-scale production processes, with the aim of improving, in particular, charge separation efficiency, photocatalytic performance, antibacterial activity, and photoelectrochemical efficiency. These goals may be achieved by controlling the crystallographic orientation and long-term stability of BiVO₄-based photoanodes. With reference to the great current concern for the preservation of the environment, the continuous exploration and optimization of BiVO₄-based structures in the field of PEC water splitting will significantly contribute to the development of a global system towards clean, renewable, and sustainable energies.

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