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# Photocatalytic Removal of Organics over BiVO<sub>4</sub>-Based Photocatalysts

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Additional information is available at the end of the chapter

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## Abstract

Organic compounds, such as organic dyes and phenols, are the main pollutants in wastewater. In the past years, a large number of studies on the fabrication and photocatalytic organics degradation of BiVO<sub>4</sub> and its related materials have been reported in the literature. In this chapter, we shall focus on the advancements in the synthesis and photocatalytic applications of several kinds of BiVO<sub>4</sub>-based photocatalysts: (i) well-defined morphological BiVO<sub>4</sub> photocatalysts, (ii) porous BiVO<sub>4</sub> photocatalysts, (iii) heteroatom-doped BiVO<sub>4</sub> photocatalysts, (iv) BiVO<sub>4</sub>-based heterojunction photocatalysts, and (v) supported BiVO<sub>4</sub> photocatalysts. We shall discuss the structure–photocatalytic performance relationship of the materials and the involved photocatalytic degradation mechanisms. In addition, we also propose the research trends and technologies for practical applications of the BiVO<sub>4</sub>-based photocatalytic materials.

**Keywords:** well-defined morphology, porous BiVO<sub>4</sub> photocatalyst, heteroatom-doped BiVO<sub>4</sub>, BiVO<sub>4</sub>-based heterojunction, supported BiVO<sub>4</sub>

## 1. Introduction

With the unceasingly expanding industrial development, environmental pollution caused by industrial effluents has nowadays become the most urgent issue to be solved [1]. In particular, various industrial processes and human activities contaminate the global water supply, which is a serious problem for living beings. During the past decades, great efforts have been made on the degradation of organic wastewater pollutants. The visible-light-driven photoca-

talysis attracts much attention, since such a photocatalytic process can directly convert organic pollutants (e.g., methylene blue (MB), methyl orange (MO), rhodamine B (RhB), phenol, and etc.) to harmless products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) under sunlight irradiation.

The organic dye models (MB, MO, and RhB) in textile and other industrial effluents have become one series of the major environmental contaminants, which have serious implications on the environment and human health [2]. Meanwhile, phenol is a widely used chemical and present in a great variety of emitted waste effluents. Organic dyes and phenol degrade slowly in the environment and are extremely toxic, carcinogenic, teratogenic, and refractory in nature [3]. Therefore, tremendous efforts have been made to fabricate high-efficiency photocatalysts for the control of wastewater pollution.

As one of the earliest studied *n*-type semiconductor photocatalysts,  $\text{TiO}_2$  has been widely used in environmental purification owing to its appropriate band position, high chemical stability, low cost, and nontoxicity [4]. However,  $\text{TiO}_2$  is only responsive to ultraviolet (UV) light owing to its wide bandgap energy (3.2 eV), which occupies no more than 4% of the solar spectrum, hence greatly restricting its practical applications [5]. Among the developed catalysts,  $\text{BiVO}_4$  is one of the most attractive photocatalysts due to its unique properties, such as ferroelasticity, photochromic effect, ionic conductivity, and visible-light responsibility [6]. It is nontoxic and has a relatively narrow bandgap energy (2.4 eV) when it is monoclinic in crystal structure. Many publications on  $\text{BiVO}_4$  describing phase structures, synthesis methods, physicochemical properties, applications, and so on have emerged since its inaugural work by Kudo et al. as a photocatalyst for  $\text{O}_2$  evolution in 1999 [7]. As a promising material,  $\text{BiVO}_4$  is extensively applied in various fields, such as gas sensors, batteries, electrolytes, water splitting, and other applications [8].

Semiconductor is a kind of materials with electrical conductivity between conductor (such as metals) and insulator (such as ceramics). The unique electronic property of a semiconductor is characterized by its valence band (VB) and conduction band (CB). The VB of a semiconductor is formed by the interaction of the highest occupied molecular orbital (HOMO), while the CB is formed by the interaction of the lowest unoccupied molecular orbital (LUMO). There is no electron state between the top of the VB and the bottom of CB. The energy range between CB and VB is called forbidden bandgap (also called bandgap energy), which is usually denoted as  $E_g$ . The band structure, including the bandgap and the positions of VB and CB, is one of the important properties for a semiconductor photocatalyst, because it determines the light absorption property as well as the redox capability of a semiconductor [9].

As shown in reaction 1, the photocatalytic reaction initiates from the generation of electron–hole pairs upon light irradiation. When a semiconductor photocatalyst absorbs photons with energy equal to or greater than its  $E_g$ , the electrons in the VB will be excited to the CB, leaving the holes in the VB. The electron-hole pairs generation process in  $\text{BiVO}_4$  can be expressed as follows:



These photogenerated electron-hole pairs may further be involved in the following three possible processes [9]: (i) successfully migrating to the surface of semiconductor, (ii) being captured by the defect sites in bulk and/or on the surface region of semiconductor, and (iii) recombining and releasing the energy in the form of heat or photon. The last two processes are generally viewed as deactivation processes because the photogenerated electrons and holes do not contribute to the photocatalytic reactions. Only the photogenerated charges that reach to the surface of semiconductor can be available for photocatalytic reactions. The defect sites in the bulk and on the surface of semiconductor may serve as the recombination centers for the photogenerated electrons and holes, which would decrease the efficiency of the photocatalytic reaction.

It is well known that the photocatalytic activity of a semiconductor depends strongly upon three factors: adsorption behavior, photoresponsive region, and separation efficiency of electron-hole pairs [10]. The adsorption behavior can usually be enhanced by improving the surface areas of catalysts. In this aspect, how to extend the photoresponsive region and improve the separation efficiency of electron-hole pairs are important factors on the photocatalytic performance of a semiconductor [11]. The way to extend the photoresponsive region of a semiconductor photocatalyst is mainly the doping of nonmetals or transition metals, which can also improve the separation efficiency of electron-hole pairs and increase the oxidation power of photogenerated carriers [12, 13]. In general, noble metals (e.g., Ag, Pt, Au, and Pd) have been used as electron acceptors to separate the photoinduced hole-electron pairs and promote the interfacial charge transfer processes [14].

Generally speaking, physicochemical properties of a material may be quite different depending on its crystal phase structure. The phase structure of BiVO<sub>4</sub> is one of the important factors determining its photocatalytic performance [15]. BiVO<sub>4</sub> has mainly three polymorphs in nature, including zircon-tetragonal, scheelite-tetragonal, and scheelite-monoclinic. The zircon-tetragonal phase can be formed via a low-temperature (100°C) synthesis route, whereas the scheelite-monoclinic phase can be generated using a high-temperature (400–600°C) synthesis method [16]. Moreover, the phase transformation between the scheelite monoclinic and the scheelite tetragonal can occur reversibly at 255°C [17]. It has been confirmed that the scheelite monoclinic structure of BiVO<sub>4</sub> is the most photocatalytically active under visible-light irradiation. The greater reactivity can be associated with the energy band structure since monoclinic and tetragonal BiVO<sub>4</sub> have bandgap energies of 2.4 and 2.9 eV, respectively. [8, 18, 19] Though BiVO<sub>4</sub> has better photocatalytic performance, various strategies have been proposed to further improve its activity. In addition to the crystal structure, the photocatalytic property also strongly depends upon the morphology of BiVO<sub>4</sub> [20]. Different morphological semiconductor photocatalysts have been prepared by many researchers. Efficient charge separation is the most important factor that determines the photocatalytic performance [9]. Furthermore, creation of heterjunction [21] and porous structure [22] as well as doping of element(s) [23] and using of support [24] are also effective strategies for improving charge separation efficiency.

## 2. Well-defined morphological BiVO<sub>4</sub> photocatalysts

As one of new photocatalysts, monoclinic BiVO<sub>4</sub> (*m*-BiVO<sub>4</sub>) with a bandgap energy of 2.4 eV has drawn great attention for its excellent performance under visible-light illumination [7, 25]. Therefore, many strategies, such as solid-state reaction, hydrothermal or solvothermal, chemical bath deposition, and solution combustion methods, are employed for the synthesis of monoclinic BiVO<sub>4</sub>. The morphology of a crystal plays a crucial role in determining its physicochemical property [26]. In recent years, scientists have been devoted to developing various synthetic routes to realize the tailored fabrication of *m*-BiVO<sub>4</sub> with different morphologies that show distinct photocatalytic properties [27]. For example, the hydrothermal method is widely used to prepare *m*-BiVO<sub>4</sub> with different morphologies because the morphology of the final product obtained via such a process can be easily controlled by changing the reaction conditions, such as reaction temperature, reaction time, solution pH, and concentration [6]. Recently, different morphologies (such as nanospheres, nanorods, nanoflowers, nanosheets, nanotubes, hyperbranched) of monoclinically structured BiVO<sub>4</sub> crystallites have been synthesized by the hydrothermal method with the assistance of surfactants and pH-controlling additives [28]. **Table 1** summarizes the physical properties and photocatalytic activities of the typical BiVO<sub>4</sub> reported in the literature.

Photocatalyst	Crystal structure	Surface area (m <sup>2</sup> /g)	<i>E<sub>g</sub></i> (eV)	Reaction condition	Degradation efficiency and light illumination time	References
Sphere-like BiVO <sub>4</sub>	Monoclinic	1.75	–	Visible light, 80 mL RhB (0.01 mmol/L), 0.1 g sample	100% and 20 min	[2]
	Monoclinic	–	–	UV light, RhB	84.1% and 2.5 h	[6]
	Monoclinic	8.4	2.45	Visible light, 200 mL MO (0.01 mmol/L), 0.1 g sample	84% and 2 h	[22]
	Monoclinic	10	2.37	Sunlight, 50 mL phenol (25 mg/L), 0.3 mL H <sub>2</sub> O <sub>2</sub> , 0.1 g sample	100% and 1.5 h	[29]
	Monoclinic	2.62	2.48	Visible light, 100 mL RhB (0.01 mmol/L), 0.08 g sample	97.7% and 6 h	[30]
	Monoclinic	–	2.5	Visible light, 100 mL RhB, 0.01 g sample	80% and 50 min	[31]
	Tetragonal	–	2.81	Sunlight, 100 mL MB (5 mg/L), 0.1 g sample	90% and 5 h	[32]
	Monoclinic	24.4	2.50	Blue light, 50 mL MB (0.01 mmol/L), 0.005 g sample	100% and 5 h	[33]
	Monoclinic	85.4	2.38	Visible light, 20 mL MB (20 mg/L), 0.02 g sample	63% and 2 h	[34]

Photocatalyst	Crystal structure	Surface area (m <sup>2</sup> /g)	E <sub>g</sub> (eV)	Reaction condition	Degradation efficiency and light illumination time	References
Flower-like BiVO <sub>4</sub>	Monoclinic	0.7	2.42	Visible light, 100 mL MB (0.01 mmol/L), 0.01 g sample	90% and 3 h	[35]
	Monoclinic	0.9	2.3	Visible light, MB (10 mg/L), 1 g/L sample	60% and 2 h	[28]
	Monoclinic	61.6	2.14	Visible light, 20 mL MB (20 mg/L), 0.02 g sample	75% and 2 h	[34]
	Monoclinic	–	2.46	Sunlight, 100 mL MO (10 mg/L), 0.5 g sample	58% and 4 h	[36]
	Monoclinic	1.6	2.45	Sunlight, 200 mL RhB (5 mg/L), 0.1 g sample	62% and 10 h	[37]
Rod-like BiVO <sub>4</sub>	Monoclinic	2.1	2.52	Visible light, 100 mL MO (0.01 mmol/L), 0.1 g sample	60% and 4 h	[38]
	Monoclinic	3.5	2.46	Sunlight, 200 mL RhB (10 mg/L), 0.2 g sample	98.3% and 8 h	[27]
	Monoclinic	4.3	2.26	Visible light, 100 mL MB (0.01 mmol/L), 0.01 g sample	90% and 2 h	[35]
	Monoclinic	3.8	2.47	Visible light, 100 mL MO (0.01 mmol/L), 0.1 g sample	87% and 4 h	[38]
	Monoclinic/tetragonal	–	2.46	Visible light, 100 mL RhB (10 mg/L), 0.04 g sample	39.5% and 2.5 h	[39]
Peanut-like BiVO <sub>4</sub>	Monoclinic	–	2.45	Visible light, 100 mL RhB (0.01 mmol/L), 0.2 g sample	96% and 50 min	[40]
	Monoclinic	10.3	2.4	Sunlight, 200 mL RhB (5 mg/L), 0.1 g sample	61% and 10 h	[37]
	Monoclinic	0.54	2.4	Solar light, 100 mL crystalviolet (0.02 mmol/L), 0.05 g sample	98% and 1 h	[41]
	Monoclinic	33.9	2.44	Visible light, 100 mL MB (10 mg/L), 0.1 g sample	95% and 225 min	[42]
	Monoclinic	5.4	2.35	UV-Vis light, 100 mL MB (10 ppm), 1 g/L sample	40% and 2 h	[43]
Polyhedron-like BiVO <sub>4</sub>	Monoclinic	0.9	2.34	Visible light, 100 mL MB (0.01 mmol/L), 0.01 g sample	90% and 2 h	[35]
	Monoclinic	3.97	2.25	Visible light, 50 mL RhB (0.015 mmol/L), 0.1 g sample	60% and 10 h	[44]
	Monoclinic	–	2.35	Visible light, 30 mL MB (5 mg/L), 0.1 g sample	81.6% and 160 min	[45]

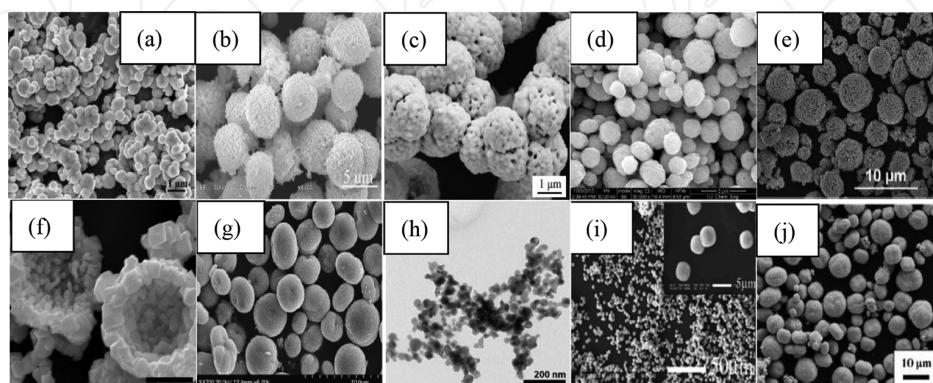
Photocatalyst	Crystal structure	Surface area (m <sup>2</sup> /g)	E <sub>g</sub> (eV)	Reaction condition	Degradation efficiency and light illumination time	References
Olive-like BiVO <sub>4</sub>	Monoclinic	0.4	2.35	Visible light,alachlor (50 mg/L), 1 g/L sample	97% and 6 h	[46]
	Monoclinic	0.91	2.40	Sunlight, 50 mL MB (10 mg/L), 0.1 g sample	18% and 3.5 h	[26]
	Monoclinic	4.6	2.40	Sunlight, 200 mL RhB (5 mg/L), 0.1 g sample	97% and 10 h	[37]
	Monoclinic	–	2.50	Visible light, 100 mL RhB (10 mg/L), 0.04 g sample	50.5% and 2.5 h	[39]
	Monoclinic	–	2.45	Visible light, 100 mL MB (10 mg/L), 0.1 g sample	67% and 225 min	[42]
Microtube-like BiVO <sub>4</sub>	Monoclinic	6.6	2.33	Visible light, 100 mL MB (0.01 mmol/L), 0.01 g sample	90% and 3 h	[35]
	Monoclinic	–	2.36	Visible light, 100 mL RhB (0.01 mmol/L), 0.5 mmol sample	96% and 3 h	[47]
	Monoclinic	0.3	2.36	Visible light, MO (20 mg/L), 0.01 g sample	95% and 3 h	[48]
	Monoclinic	3.46	2.48	Visible light, 100 mL RhB (0.01 mmol/L), 0.2 g sample	100% and 5 h	[49]
Dumbbell-like BiVO <sub>4</sub>	Monoclinic	4.6	2.43	Visible light, 200 mL RhB (5 mg/L), 0.1 g sample	89% and 10 h	[37]
	Monoclinic	–	2.51	Visible light, 600 mL RhB (0.01 mmol/L), 0.3 g sample	90% and 4.5 h	[50]
	Monoclinic	9.87	2.25	Sunlight, 100 mL ofloxacin (20 mg/L), 0.1 g sample	80.8% and 1 h	[51]
	Monoclinic	53.6	2.42	Visible light, 100 mL RhB (0.01 mmol/L), 0.1 g sample	100% and 1 h	[52]
Needle-like BiVO <sub>4</sub>	Monoclinic	–	–	Sunlight, 200 mL RhB (5 mg/L), 0.1 g sample	40% and 10 h	[37]
	Monoclinic	2.0	2.41	UV–Vis light, MB (10 ppm), 1 g/L sample	60% and 2 h	[43]
	Monoclinic	17.63	2.42	Visible light, 100 mL MB (10 mg/L), 0.005 g sample	81% and 200 min	[53]
	Monoclinic	1.6	2.38	UV–Vis light, MB (10 ppm), 1 g/L sample	66% and 3 h	[54]
Dendrite-like BiVO <sub>4</sub>	Monoclinic/tetragonal	1.88	2.52	Visible light, 100 mL MB (20 mg/L), 0.1 g sample	95% and 3 h	[16]

Photocatalyst	Crystal structure	Surface area (m <sup>2</sup> /g)	E <sub>g</sub> (eV)	Reaction condition	Degradation efficiency and light illumination time	References
Butterfly-like BiVO <sub>4</sub>	Monoclinic	1.22	2.34	Sunlight, 50 mL MB (10 mg/L), 0.1 g sample	74.8% and 3.5 h	[26]
Nanosheet-like BiVO <sub>4</sub>	Monoclinic	–	3.3	Visible light, 100 mL RhB, 0.01 g sample	50% and 50 min	[31]
Leaf-like BiVO <sub>4</sub>	Monoclinic	3.0	2.34	Visible light, 100 mL MB (0.01 mmol/L), 0.01 g sample	100% and 3 h	[35]
Cuboid-like BiVO <sub>4</sub>	Monoclinic	–	2.39	Sunlight, 100 mL MO (10 mg/L), 0.5 g sample	36% and 4 h	[36]
Star-like BiVO <sub>4</sub>	Monoclinic	–	2.44	Visible light, 100 mL MB (10 mg/L), 0.1 g sample	76% and 225 min	[42]
Bone-like BiVO <sub>4</sub>	Monoclinic	10.32	2.36	Visible light, 100 mL MB (0.01 mmol/L), 0.005 g sample	61% and 200 min	[53]

**Table 1.** Physical properties and photocatalytic activities of the well-defined morphological BiVO<sub>4</sub> photocatalysts.

## 2.1. Sphere-like BiVO<sub>4</sub>

Among different morphologies of BiVO<sub>4</sub>, microspherical or nanospherical BiVO<sub>4</sub> particles are mostly reported. For example, Kunduz et al. [29] reported the preparation of monoclinic bismuth vanadate catalysts by hydrothermal method at different pH values and the removal of phenol from wastewater under natural sunlight illumination. Homogenous and spherical BiVO<sub>4</sub> (particle size = 40–90 nm) was formed at pH = 2 (**Figure 1d**), the bandgap energy of the BiVO<sub>4</sub> sample calculated from the absorption edge was 2.37 eV. This BiVO<sub>4</sub> sample showed a high phenol conversion (100%) within 90 min of natural sunlight illumination, which was related to the morphology of BiVO<sub>4</sub> (surface area = 10 m<sup>2</sup>/g).



**Figure 1.** (a–g, i, j) SEM and (h) TEM images of sphere-like BiVO<sub>4</sub>: (a) [2], (b) [6], (c) [22], (d) [29], (e) [30], (f) [31], (g) [32], (h) [33], (i) [34], and (j) [35].

An one-pot template-free hydrothermal method was developed for the fabrication of  $\text{BiVO}_4$  microspheres with a tetragonal–monoclinic heterophasic structure [30]. The average diameter, bandgap energy, and BET surface area of the as-prepared  $\text{BiVO}_4$  microspheres were 4–6  $\mu\text{m}$ , 2.48 eV, and 2.62  $\text{m}^2/\text{g}$ , respectively. The  $\text{BiVO}_4$  microspheres exhibited the highest photocatalytic activity with ca. Ninety-eight percentage degradation of RhB, remarkably superior to the pure monoclinic–scheelite  $\text{BiVO}_4$  and tetragonal–zircon  $\text{BiVO}_4$ . The enhanced photocatalytic performance was attributed to the more effective separation of photogenerated carriers generated in the heterophasic  $\text{BiVO}_4$ . Based on free radical scavenging and  $\text{N}_2/\text{O}_2$ -purging experiments, the degradation of RhB was believed to be driven mainly by the participation of  $\cdot\text{O}_2^-$  and a lesser extent by the participation of holes and  $\cdot\text{OH}$ .

Sun et al. [31] prepared monoclinic scheelite  $\text{BiVO}_4$  hollow spheres (diameter = 3000–4000 nm) using a simple hydrothermal method with urea as guiding surfactant. It is observed that the RhB removal efficiency of  $\text{BiVO}_4$  hollow spheres was more than 80% after 50 min of visible-light irradiation without adding any  $\text{H}_2\text{O}_2$ . The superior activity of the *m*- $\text{BiVO}_4$  sample was attributed to two reasons: (i) the BET surface area of the hierarchical hollow spheres was 10.6  $\text{m}^2/\text{g}$ , the higher surface area provided not only more surface reached by the visible light but also more active sites, which would result in good photocatalytic performance and (ii) the large hollow space inside the microspheres greatly decreased the density of *m*- $\text{BiVO}_4$ , thus rendering them to be easily suspended in water.

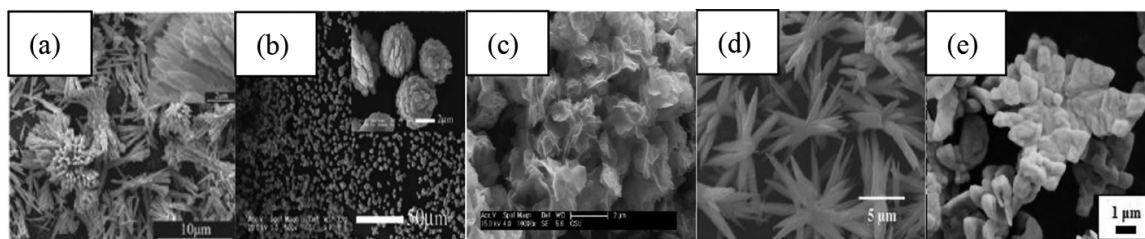
Monoclinic  $\text{BiVO}_4$  crystals with a particle size of 400–700 nm and a surface area of 1.75  $\text{m}^2/\text{g}$  were synthesized with the assistance of cetyltrimethylammonium bromide (CTAB) [2]. The given RhB solution (100 mL,  $10^{-5}$  M) was completely degraded within 20 min of visible-light irradiation, which was due to the addition of CTAB during the catalyst fabrication process.

Many other researchers also reported various kinds of spherical  $\text{BiVO}_4$  crystallites (Table 1). For example, Ma et al. [32] prepared  $\text{BiVO}_4$  microspheres by a hydrothermal method in the presence of ethylenediamine tetraacetic acid (EDTA) for the removal of MB under sunlight illumination. Jiang et al. [22] reported porous spherical  $\text{BiVO}_4$  using urea as pH adjustor and polyvinyl pyrrolidone (PVP) as surfactant for MO degradation. Castillo et al. [33] studied flame-assisted synthesis of nanoscale spherical  $\text{BiVO}_4$  for the degradation of MB under visible-light illumination. These spherical  $\text{BiVO}_4$  samples exhibited good photocatalytic activities for the degradation of organic dyes under visible-light irradiation.

## 2.2. Flower-like $\text{BiVO}_4$

A flower-like morphology is usually composed of nanorods or nanosheets. Flower-like particles not only look beautiful, but also show good photocatalytic performance. Fan et al. [34] prepared monoclinic  $\text{BiVO}_4$  with a flower-like morphology via a simple hydrothermal route by adjusting the amount of surfactant (PVP K30). The photocatalytic efficiency for the decolorization of MB aqueous solution could reach 75% in 2 h of visible-light irradiation. The UV-visible diffuse reflectance absorption spectra reveal that this  $\text{BiVO}_4$  sample showed excellent absorption of visible light in the region of up to 600 nm, and the  $E_g$  was 2.14 eV. The flower-like sample was composed of numerous  $\text{BiVO}_4$  sub-nanoparticles (400–500 nm)

(Figure 2). The BiVO<sub>4</sub> possessed a small size, a narrow bandgap energy, and a high BET surface area (61.6 m<sup>2</sup>/g), which facilitated the enhancement of photocatalytic activity.



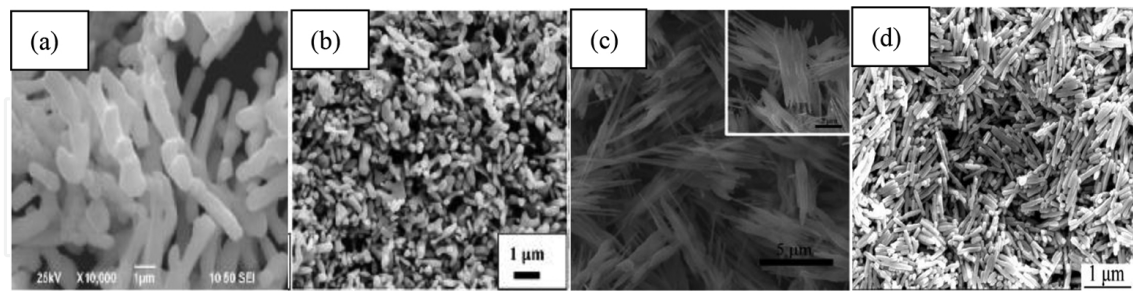
**Figure 2.** SEM images of flower-like BiVO<sub>4</sub>: (a) [28], (b) [34], (c) [36], (d) [37], and (e) [38].

An *m*-BiVO<sub>4</sub> sample with a regular morphology was prepared using a facile hydrothermal method with Bi<sub>2</sub>O<sub>3</sub> and NH<sub>4</sub>VO<sub>3</sub> as starting material [36]. The as-synthesized sample had a flower-like structure with a diameter of 1–2 μm and a bandgap energy of 2.46 eV. About 58% of MO in the aqueous solution was degraded after sunlight irradiation for 4 h. Photocatalytic performance of the as-prepared BiVO<sub>4</sub> sample was much better than that of P25 under the same reaction conditions, which might be ascribable to the flower structure and the larger surface area of the nanosheet-like BiVO<sub>4</sub> sample. Larger surface area can facilitate the harvesting of light, whereas the thinness of the nanosheets can cause a bigger distortion of the unit cell induced by the large surface strain. All of those factors might contribute to the improvement in photocatalytic activity of BiVO<sub>4</sub>.

### 2.3. Rod-like BiVO<sub>4</sub>

**Figure 3** shows the scanning electron microscopic (SEM) images of the rod-like BiVO<sub>4</sub> samples. Hu et al. [27] reported the controlled fabrication of monoclinic BiVO<sub>4</sub> with a rod-like structure and investigated the effect of calcination temperature on the sunlight-driven photocatalytic degradation of RhB. It is found that the sample calcined at 300°C exhibited a superior photocatalytic activity: RhB at an initial concentration of RhB lower than 10 mg/L could be completely decolorized after 6 h of sunlight irradiation. The bandgap energy and BET surface area of the rod-like BiVO<sub>4</sub> photocatalyst were 2.46 eV and 3.5 m<sup>2</sup>/g, respectively. It can be observed from the SEM images (Figure 3) that the sample obtained after calcination at 300°C was composed of dispersive and short rod-like nanocrystals, thus displaying higher BET surface area, which would enhance the adsorption ability and hence improve the photocatalytic performance. Dai and coworkers [35] prepared monoclinic BiVO<sub>4</sub> single crystallites with different morphologies using the triblock copolymer P123-assisted hydrothermal strategy with bismuth nitrate and ammonium metavanadate as metal source and various bases as pH adjustor. The rod-like BiVO<sub>4</sub> sample was obtained at pH = 6 using NH<sub>3</sub>–H<sub>2</sub>O as pH adjustor. This sample displayed a higher surface area (3.2 m<sup>2</sup>/g) and a lower bandgap energy (2.26 eV). The rod-like BiVO<sub>4</sub> sample showed excellent visible-light-driven photocatalytic activity for MB degradation in an aqueous solution under visible light irradiation: 90% degradation was achieved within 2 h of reaction. The unusually high visible-light-driven catalytic performance of monoclinically crystallized rod-like BiVO<sub>4</sub> single crystallite was associated with its

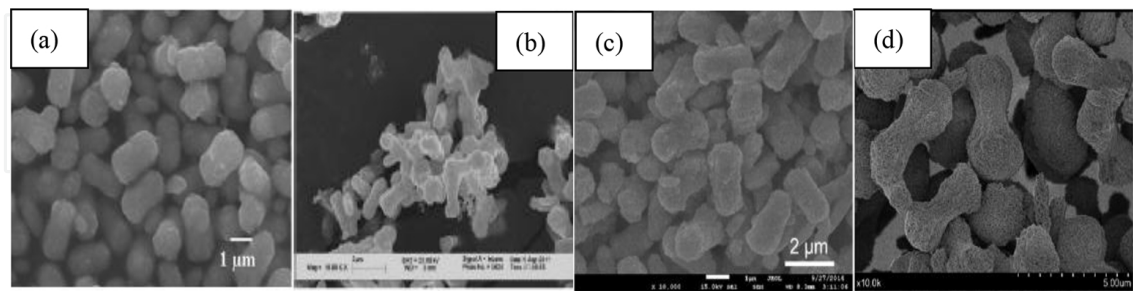
higher surface area and surface oxygen defect concentrations as well as the unique particle morphology.



**Figure 3.** SEM images of rod-like  $\text{BiVO}_4$ : (a) [27], (b) [35], (c) [39], and (d) [40].

**2.4. Peanut-like  $\text{BiVO}_4$**

Chen et al. [41] synthesized *m*- $\text{BiVO}_4$  with a hollow peanut-like morphology (**Figure 4b**) using L-lysine as surfactant, and studied its photocatalytic activity for the degradation of crystal violet under solar light irradiation. The best performance was observed over the sample crystallized at 160°C in the presence of L-lysine and after calcination at 550°C. Ninety-eight percentage of the crystal violet could be removed after exposure for 1 h. Although the surface area decreased with the rise in calcination temperature [2.0  $\text{m}^2/\text{g}$  (at 350°C), 0.86  $\text{m}^2/\text{g}$  (at 450°C), and 0.54  $\text{m}^2/\text{g}$  (at 550°C)], their bandgap energies were about 2.4 eV, and the sample calcined at 550°C performed better than the one calcined at 450 or 350°C. The authors assigned the good photocatalytic activity of *m*- $\text{BiVO}_4$  to its unique hollow peanut-like morphology and pure monoclinic phase of high crystallinity, rather than to the bandgap energy and surface area. The physical properties and photocatalytic activities of several kinds of peanut-like  $\text{BiVO}_4$  samples reported in the literature are listed in **Table 1**.

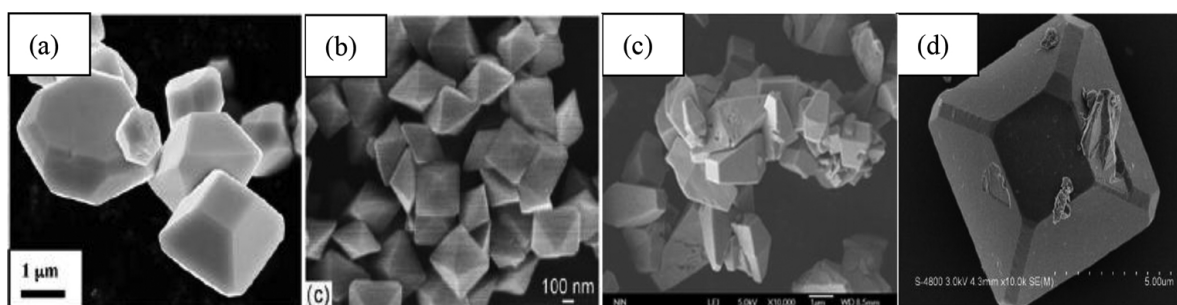


**Figure 4.** SEM images of peanut-like  $\text{BiVO}_4$ : (a) [37], (b) [41], (c) [42], and (d) [43].

**2.5. Polyhedron-like  $\text{BiVO}_4$**

The physical properties and photocatalytic activities of the related polyhedral  $\text{BiVO}_4$  samples are summarized in **Table 1**. For example, Han et al. [44] reported the synthesis of

monodispersed octahedral *m*-BiVO<sub>4</sub> nanocrystals via a simple hydrothermal route in the presence of sodium dodecyl benzene sulfonate (SDBS). The octahedral *m*-BiVO<sub>4</sub> nanocrystal with a size of 200–300 nm (**Figure 5b**) exhibited the highest photocatalytic activity (RhB was completely degraded within 10 h of visible-light irradiation). The octahedral crystals displayed higher surface area (3.97 m<sup>2</sup>/g) and narrower bandgap energy (2.25 eV). Such a good photocatalytic activity was attributed to the good crystallization with fewer structural defects and preferred crystal facets for surface-controlled photocatalysis as well as the better optical absorption property and higher surface area. Zhu et al. [45] has successfully synthesized monoclinic decahedral BiVO<sub>4</sub> by the microwave-assisted hydrothermal method with Tween-80 as template. The photocatalytic efficiency of decahedral BiVO<sub>4</sub> obtained hydrothermally at 160°C showed the highest photocatalytic MB degradation efficiency (ca. 82% MB was degraded after 160 min of visible-light irradiation). The bandgap energy of the sample derived hydrothermally at 160°C was 2.35 eV. The authors concluded that the good photocatalytic performance of the decahedral BiVO<sub>4</sub> sample was related to the imperfect crystal and small size, which resulted in the efficient separation of the electron–hole pairs.

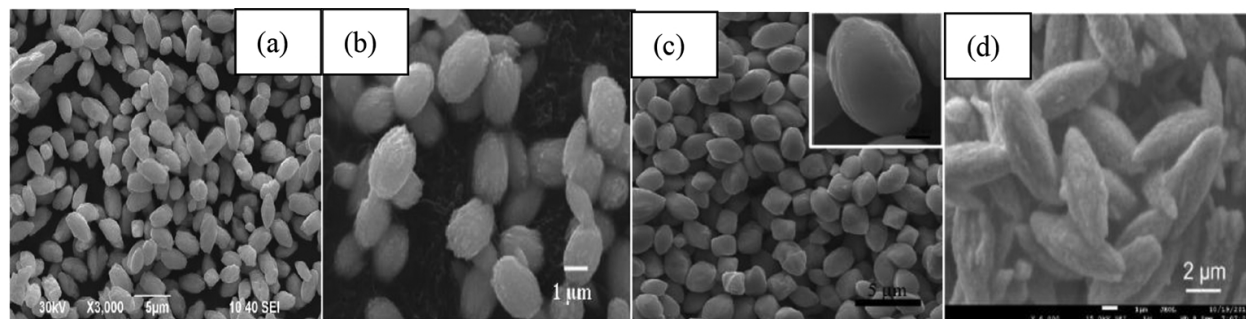


**Figure 5.** SEM images of polyhedron-like BiVO<sub>4</sub>: (a) [35], (b) [44], (c) [45], and (d) [46].

## 2.6. Olive-like BiVO<sub>4</sub>

The physical properties and photocatalytic activities of several kinds of olive-like BiVO<sub>4</sub> samples are listed in Table 1. Adopting the facile pH-dictated solvothermal route with the aid of either NH<sub>3</sub>–H<sub>2</sub>O or NaOH, Dong et al. [37] controllably synthesized the uniform monoclinic scheelite BiVO<sub>4</sub> with hierarchical structures. As the pH value was adjusted to 6.26 using NaOH as the pH controller, the olive-like BiVO<sub>4</sub> crystallites (bandgap energy = 2.40 eV) was generated. The olive-like BiVO<sub>4</sub> sample showed a RhB degradation efficiency of 97% after 10 h of sunlight irradiation. It should be noted that this sample did not have a high surface area (4.6 m<sup>2</sup>/g) in comparison with other samples (surface area = 6.3–11.1 m<sup>2</sup>/g) obtained at different pH values. Apparently, the enhanced photocatalytic performance was not related to the surface area and aspect ratios of the fabricated photocatalysts, but to the unique morphological configurations. Lei et al. [39] synthesized olive-like BiVO<sub>4</sub> using a hydrothermal strategy at pH = 3.0. As seen from the SEM images (**Figure 6c**), the sizes of the BiVO<sub>4</sub> particles were predominantly 1.8–2.9 μm in length and 1.1–1.8 μm in diameter. The olive-like BiVO<sub>4</sub> photocatalyst with a bandgap energy of 2.5 eV showed the highest photocatalytic activity,

which could photocatalytically degrade 50.5% RhB after 150 min of visible-light illumination. The synergic effect of monoclinic phase and particle size contributed to the high photocatalytic efficiency of the olive-like  $\text{BiVO}_4$  photocatalyst.

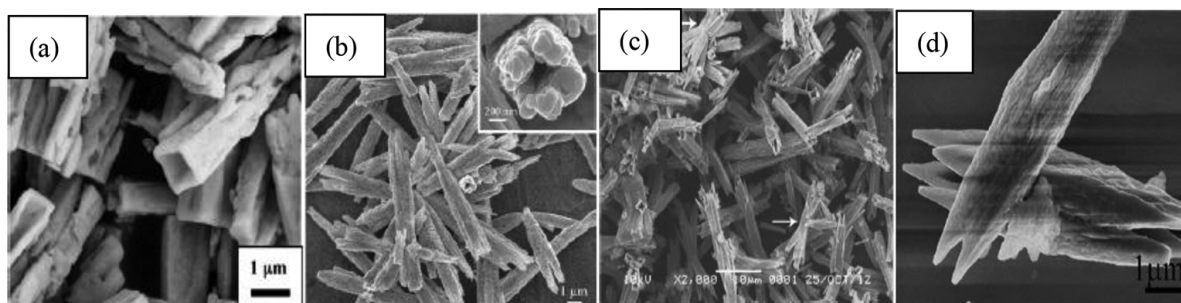


**Figure 6.** SEM images of olive-like  $\text{BiVO}_4$ : (a) [26], (b) [37], (c) [39], and (d) [42].

Dai and coworkers [38] fabricated the  $\text{BiVO}_4$  samples with a monoclinic scheelite-type structure and various morphologies via an alcohol-hydrothermal route with  $\text{Bi}(\text{NO}_3)_3$  and  $\text{NH}_4\text{VO}_3$  as precursor and sodium hydroxide as pH adjustor in the absence or presence of triblock copolymer P123. It is realized that the pH of the precursor solution and the surfactant greatly affected the particle shape and architecture of  $\text{BiVO}_4$ . Porous  $\text{BiVO}_4$  particles with spherical, flower-like, and sheet-like shapes were obtained in the presence of P123 at a reaction temperature of  $180^\circ\text{C}$  and a pH of 2, 7, or 10, respectively. A rod-like  $\text{BiVO}_4$  was generated at reaction temperature =  $180^\circ\text{C}$  and pH = 2. The four  $\text{BiVO}_4$  samples possessed a surface area of  $1.4\text{--}3.8\text{ m}^2/\text{g}$  and a bandgap energy of  $2.47\text{--}2.54\text{ eV}$ . The difference in morphology of the  $\text{BiVO}_4$  particles gave rise to discrepancies in surface area, surface oxygen deficiency density, and (040) crystal face exposure. The rod-like  $\text{BiVO}_4$  sample that possessed the largest surface area, the highest surface oxygen deficiency density, the highest (040) crystal face exposure, and the lowest bandgap energy performed the best for MO degradation under visible-light irradiation. It is concluded that the particle morphology could influence the photocatalytic activity of  $\text{BiVO}_4$  and the rod-like shape was favorable for the improvement in photocatalytic activity.

## 2.7. Microtube-like $\text{BiVO}_4$

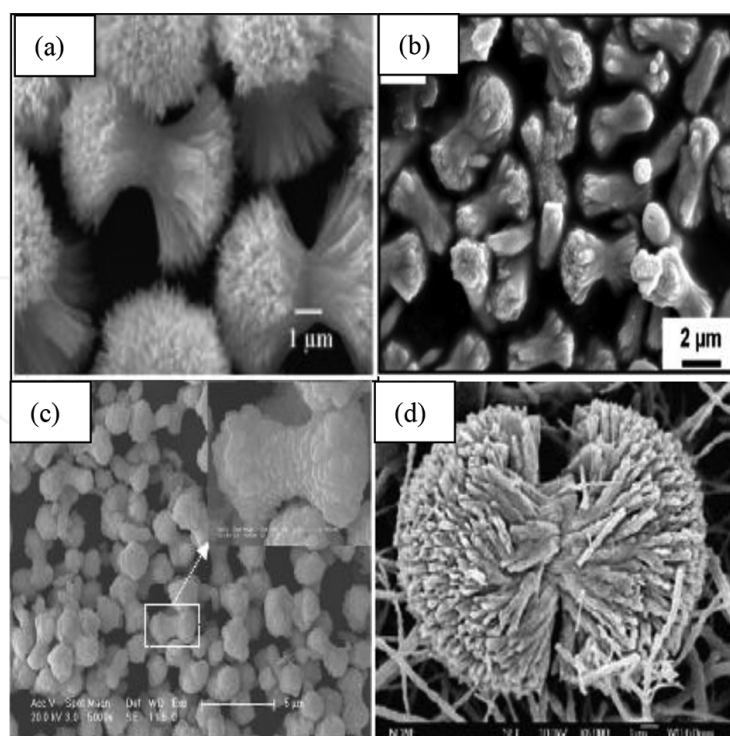
The physical properties and photocatalytic activities of tubular  $\text{BiVO}_4$  samples reported in the literature are summarized in **Table 1**. Single-crystalline monoclinic  $\text{BiVO}_4$  microtubes with a side length of 800 nm and a wall thickness of 100 nm (**Figure 7b**) were synthesized by a facile reflux method at  $80^\circ\text{C}$  [47]. The results of optical absorption experiments reveal that in addition to the UV light region, the  $\text{BiVO}_4$  microtubes also had a strong absorption in the visible-light region and the bandgap energy was estimated to be 2.36 eV. The RhB photodegradation over the  $\text{BiVO}_4$  microtubes was up to 96% after 3 h of visible-light irradiation, which could be associated with its distinctive morphology.



**Figure 7.** SEM images of microtube-like BiVO<sub>4</sub>: (a) [35], (b) [47], (c) [48], and (d) [49].

## 2.8. Dumbbell-like BiVO<sub>4</sub>

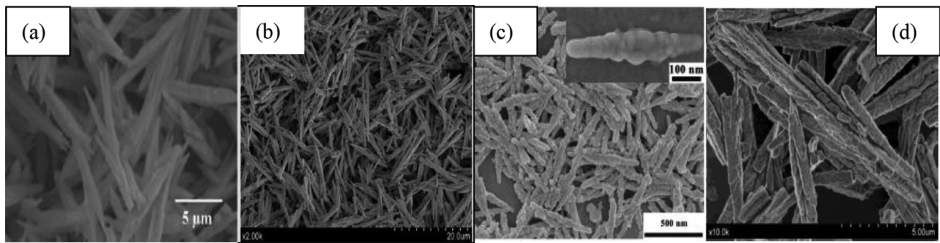
Lu et al. [50] reported the controllable synthesis of dumbbell-like BiVO<sub>4</sub> with a hierarchical nanostructure (**Figure 8b**) and a bandgap energy of 2.51 eV by employing a simple hydrothermal process. The photocatalytic degradation of RhB over the dumbbell-like BiVO<sub>4</sub> sample was up to 90% within 4.5 h of visible-light irradiation, which was much higher than the P25 sample under the same reaction conditions. The good visible-light-driven photocatalytic efficiency was related to the exposed crystal planes, which could not only provide more active sites for the photocatalytic reaction but also effectively promote the separation efficiency of the electron–hole pairs. The physical properties and photocatalytic activities of several kinds of dumbbell-like BiVO<sub>4</sub> samples reported in the literature are summarized in **Table 1**.



**Figure 8.** SEM images of dumbbell-like BiVO<sub>4</sub>: (a) [37], (b) [50], (c) [51], and (d) [52].

2.9. Needle-like BiVO<sub>4</sub>

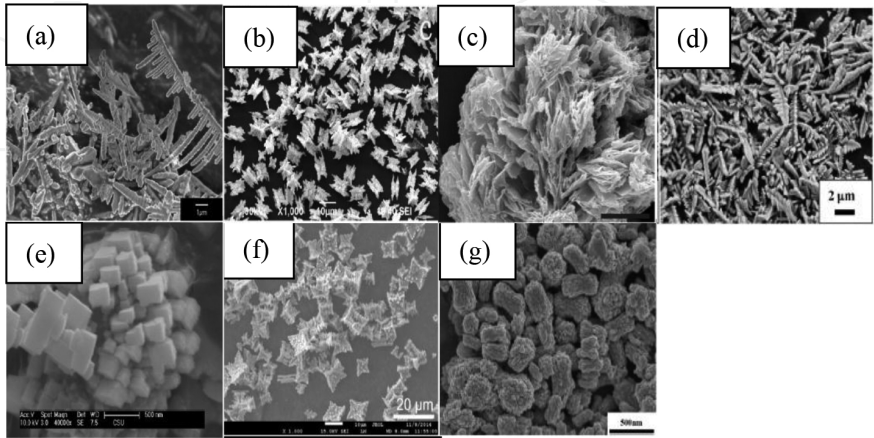
The physical properties and photocatalytic activities of the typical needle-like BiVO<sub>4</sub> samples are summarized in **Table 1**. For example, Obregón et al. [43] prepared monoclinic BiVO<sub>4</sub> with different morphologies by a surfactant-free hydrothermal method through adjusting the pH value, precipitating agent type, hydrothermal temperature, and treatment time. The needle-like particles (**Figure 9b**) obtained with hydrothermal treatment at 100°C and NH<sub>4</sub>OH as pH controlling agent showed the best efficiency (50–60% after 2 h of UV-visible-light irradiation) for MB photodegradation. The surface areas of the samples obtained with hydrothermal treatment time of 2, 8, and 20 h were 30.2, 2.7, and 1.6 m<sup>2</sup>/g, respectively. It should be noted that the slight diminution in surface area had no clear effect on the photocatalytic performance of the sample. Therefore, the best performance was not associated with the surface area, but strongly affected by the crystallite size and morphology.



**Figure 9.** SEM images of needle-like BiVO<sub>4</sub>: (a) [37], (b) [43], (c) [53], and (d) [54].

2.10. BiVO<sub>4</sub> with other morphologies

In addition to the well-morphological BiVO<sub>4</sub> samples described above, there are some kinds of BiVO<sub>4</sub> samples with other morphologies (**Figure 10**) that have been prepared. Most of them perform well in the photocatalytic degradation of organic dyes (**Table 1**).



**Figure 10.** SEM images of BiVO<sub>4</sub> with various morphologies: (a) [16], (b) [26], (c) [31], (d) [35], (e) [36], (f) [42], and (g) [53].

### 3. Porous BiVO<sub>4</sub> photocatalysts

Most of the monoclinic BiVO<sub>4</sub> samples obtained using the above methods are bulk materials and are low in surface area (<4 m<sup>2</sup>/g) [55, 56], which is unfavorable for photocatalytic applications. The reasons are as follows: (i) the amount of surface active sites is intimately related to the surface area [57, 58] and (ii) a porous architecture can increase the ability to capture incident light and the transfer of reactant and product molecules [59]. Therefore, it is of significance to controllably prepare BiVO<sub>4</sub> photocatalysts that are porous in structure and high in surface area. The physical properties and photocatalytic activities of typical porous BiVO<sub>4</sub> samples are summarized in **Table 2**.

Photocatalyst	Crystal structure	Crystallite size (nm)	Surface area (m <sup>2</sup> /g)	E <sub>g</sub> (eV)	Reaction condition	Degradation efficiency and light illumination time	References
3DOM BiVO <sub>4</sub>	Monoclinic	185	23.6	2.50	Visible light, 200 mL phenol (0.1 mmol/L), 0.2 g sample	94% and 3 h	[3]
Mesoporous BiVO <sub>4</sub>	Monoclinic	–	8.4	2.45	Visible light, 200 mL MO (0.01 mmol/L), 0.1 g sample	84% and 2 h	[22]
Ordered mesoporous BiVO <sub>4</sub>	Monoclinic	3.5	59	2.20	Visible light, 80 mL MB (10 ppm), 0.08 g sample	85% and 3h	[57]
Mesoporous BiVO <sub>4</sub>	Monoclinic	–	11.8	2.38	Visible light, 200 mL phenol (0.2 mmol/L), 0.2 g sample	91% and 4 h	[60]
Mesoporous BiVO <sub>4</sub>	Monoclinic	2.2	7.2	2.38	Sunlight, 200 mL RhB (0.02 mmol/L), 0.2 g sample	100% and 1 h	[61]
3DOM InVO <sub>4</sub>	Monoclinic	130–140	52.3	2.50	Visible light, 100 mL MB (10 mg/L), 0.1 g sample	98% and 1 h	[62]
15 wt% CrO <sub>2</sub> /InVO <sub>4</sub>	Monoclinic	155–165	45	2.10	Visible light, 100 mL RhB (15 mg/L), 0.1 g sample	99% and 200 min	[63]
0.08 wt% Au/3DOM InVO <sub>4</sub> –BiVO <sub>4</sub>	Monoclinic	22.3	25.1	2.54	Visible light, 100 mL RhB (15 mg/L), 0.1 g sample	100% and 50 min	[64]
0.08 wt% Au/3DOM InVO <sub>4</sub> –BiVO <sub>4</sub>	Monoclinic	22.3	25.1	2.54	Visible light, 100 mL MB (20 mg/L), 0.1 g sample	100% and 90 min	[64]
0.08 wt% Au/3DOM InVO <sub>4</sub> –BiVO <sub>4</sub>	Monoclinic	22.3	25.1	2.54	Visible light, 100 mL RhB (15 mg/L) + MB (20 mg/L), 0.1 g sample	100% and 120 min	[64]
0.17 wt% Pd/10 wt % AgBr/BiVO <sub>4</sub>	Monoclinic	29.8	12.9	2.49	Visible light, 100 mL 4-chlorophenol (15 mg/L), 0.05 g sample	100% and 2.5 h	[65]

**Table 2.** Physical properties and photocatalytic activities of the porous BiVO<sub>4</sub> photocatalysts.

By adopting an alcohol-hydrothermal method with  $\text{Bi}(\text{NO}_3)_3$  and  $\text{NH}_4\text{VO}_3$  as precursor, sodium hydroxide as pH adjustor, ethanol and ethylene glycol as solvent, and dodecylamine, oleylamine, or oleic acid as surfactant, Dai and coworkers [59] prepared the  $\text{BiVO}_4$  materials with various shapes and/or mesoporous architectures. Photocatalytic activities of the as-derived samples were measured for phenol degradation in the presence of  $\text{H}_2\text{O}_2$  under visible-light illumination, and effect of phenol concentration on photocatalytic performance was also probed. The authors pointed out that the surfactant and pH exerted a significant impact on particle morphology and crystal phase structure of  $\text{BiVO}_4$ . Monoclinic  $\text{BiVO}_4$  samples with a porous olive-like shape could be fabricated with dodecylamine, oleylamine, or oleic acid as surfactant at a pH of 1.5 or 3.0 and a reaction temperature of  $100^\circ\text{C}$ . Short-rod-like monoclinic  $\text{BiVO}_4$  and porous sheet-layered spherical orthorhombic  $\text{Bi}_4\text{V}_2\text{O}_{11}$  were generated with dodecylamine as surfactant at reaction temperature =  $100^\circ\text{C}$  and pH = 7.0 and 11.0, respectively. Among all of the as-prepared  $\text{BiVO}_4$  samples, the porous sample with an olive-like morphology and a surface area of  $12.7 \text{ m}^2/\text{g}$  (derived with dodecylamine and at pH = 1.5) exhibited the best visible-light-driven photocatalytic performance for phenol degradation (96% phenol was removed within 4 h of visible-light illumination).

Jiang et al. [60] prepared monoclinic  $\text{BiVO}_4$  single crystallites with a porous octapod-like morphology using the P123-assisted hydrothermal method with bismuth nitrate and ammonium metavanadate as metal source and various bases as pH adjustor. The  $\text{BiVO}_4$  with a surface area of  $11.8 \text{ m}^2/\text{g}$  and a bandgap energy of 2.38 eV showed excellent photocatalytic activities for the degradation of MB and phenol. Near 100 and 91% degradation of MB and phenol were achieved within 2 and 4 h of visible-light irradiation, respectively. The authors concluded that the high visible-light-driven catalytic performance of the porous octapod-like  $\text{BiVO}_4$  single crystallites was associated with the higher surface area, porous structure, and lower bandgap energy.

Peanut-shaped porous monoclinic  $\text{BiVO}_4$  with high yield was prepared using a simple template-free solvothermal method [61]. The pore size of the sample was 2.2 nm. Compared to the  $\text{BiVO}_4$  sample obtained hydrothermally, the porous  $\text{BiVO}_4$  sample exhibited a higher photocatalytic activity for the degradation of RhB and maintained high catalytic efficiency in the repeated recycles of the  $\text{H}_2\text{O}_2$ -containing system. Nearly, complete degradation of RhB was observed after 1 h of sunlight irradiation. It is noteworthy that the bandgap energy (2.38 eV) of the porous  $\text{BiVO}_4$  sample was higher than that (2.28 eV) of the nonporous  $\text{BiVO}_4$  sample, but the surface area ( $7.3 \text{ m}^2/\text{g}$ ) of the former was considerably higher than that ( $2.1 \text{ m}^2/\text{g}$ ) of the latter.

Li et al. [57] prepared ordered mesoporous monoclinic  $\text{BiVO}_4$  using mesoporous silica (KIT-6) as template. The mesoporous  $\text{BiVO}_4$  sample had a surface area of  $59 \text{ m}^2/\text{g}$  and a pore size of 3.5 nm. The mesoporous  $\text{BiVO}_4$  exhibited a superior visible-light-driven photocatalytic activity for the degradation of MB. The degradation rate over the mesoporous  $\text{BiVO}_4$  sample was twice as active as the conventional  $\text{BiVO}_4$  sample, and 85% MB could be degraded after 3 h of visible-light illumination. The mesoporous  $\text{BiVO}_4$  sample possessed a large surface area, an ordered structure, and a small crystal size, thus resulting in excellent visible-light photocatalytic

activity. The most attractive feature of the mesoporous BiVO<sub>4</sub> semiconductor with a bandgap energy of 2.20 eV was its excellent visible-light response ability.

Liu et al. [3] prepared three-dimensionally ordered macroporous (3DOM) bismuth vanadates with a monoclinic crystal structure and high surface areas (18–24 m<sup>2</sup>/g) using ascorbic acid-assisted poly(methyl methacrylate) (PMMA)-templating strategy. The average macropore size and wall thicknesses of the BiVO<sub>4</sub> samples were in the ranges of 160–185 and 24–70 nm, respectively. The photocatalytic performance of the porous BiVO<sub>4</sub> samples was evaluated for the degradation of phenol in the presence of a small amount of H<sub>2</sub>O<sub>2</sub> under visible-light illumination. The results showed that the conversion of phenol could reach 94% at an initial phenol concentration of 0.1 mmol/L after 3 h of visible-light irradiation. However, only 51% phenol was degraded over the bulk BiVO<sub>4</sub> sample. The authors concluded that the excellent photocatalytic activity of 3DOM BiVO<sub>4</sub> was associated with the high-quality 3DOM-structured BiVO<sub>4</sub> that has a high surface area and a surface oxygen vacancy density.

Wang et al. [62] reported the 3DOM-structured monoclinic InVO<sub>4</sub> with high surface areas (35–52 m<sup>2</sup>/g) using the citric acid-, tartaric acid-, or ascorbic acid-assisted PMMA-templating strategy. From the SEM images, among the as-obtained samples, the InVO<sub>4</sub> sample derived with PMMA in the presence of ascorbic acid showed the best quality in 3DOM architecture and a bandgap energy of 2.50 eV, with the macropore and nanovoid (on the skeletons) sizes being in the ranges of 130–160 and of 2–10 nm, respectively. Ninety-eight percentage MB was removed over the ascorbic acid-derived sample within 1 h of visible-light illumination. It is concluded that the excellent photocatalytic activity of this sample was related to its higher surface area and surface oxygen vacancy density and lower bandgap energy as well as the better quality of 3DOM structure.

Dai and coworker [63] loaded certain amounts of chromia on the surface of 3DOM InVO<sub>4</sub> to obtain the *y*CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub> (*y* = 5, 10, 15, and 20 wt%) photocatalysts. They investigated the photocatalytic degradation of RhB in the presence of H<sub>2</sub>O<sub>2</sub> under visible-light illumination and found that (i) chromia in the *y*CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub> samples were highly dispersed on the surface of 3DOM InVO<sub>4</sub>; (ii) after loading of CrO<sub>*x*</sub>, the surface areas of the *y*CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub> samples decreased; (iii) after visible-light illumination for 200 min, the RhB conversion was 47% over 3DOM InVO<sub>4</sub>, 90% over 5CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub>, 96% over 10CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub>, 97% over 20CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub>, and 99% over 15CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub>; (iii) the *y*CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub> samples exhibited stronger absorption in the UV- and visible-light than the 3DOM InVO<sub>4</sub>; (iv) the *y*CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub> samples possessed higher amounts of surface oxygen vacancies than the 3DOM InVO<sub>4</sub> sample. These authors concluded that the good visible-light-driven catalytic activity of 15CrO<sub>*x*</sub>/3DOM InVO<sub>4</sub> was associated with its CrO<sub>*x*</sub> loading, higher surface area and surface oxygen vacancy density, and lower bandgap energy as well as the better quality of 3DOM structure.

Ji et al. [64] prepared the 3DOM InVO<sub>4</sub>-BiVO<sub>4</sub> (InBi-3D) and its supported noble metal (*M*) nanoparticles (0.17 wt% *M*/InBi-3D, *M* = Au, Ag, Pd, Pt) using the PMMA-templating and polyvinyl alcohol (PVA)- or PVP-assisted reduction methods, respectively. There was co-presence of orthorhombic InVO<sub>4</sub> and monoclinic BiVO<sub>4</sub> in the InBi-3D or *M*/InBi-3D samples. The as-fabricated samples displayed a surface area of 17–30 m<sup>2</sup>/g, a *M* particle size of 2.5–3.8

nm, and a bandgap energy of 2.50–2.56 eV. The 0.08 wt% Au/InBi-3D sample exhibited the best photocatalytic activity: The complete degradation of RhB, MB, and RhB + MB could be achieved within 50, 90, and 120 min of visible-light illumination. The authors believe that the 3DOM hierarchical architecture,  $\text{InVO}_4\text{--BiVO}_4$  composite, and high dispersion of plasmonic gold nanoparticles were the main factors responsible for excellent photocatalytic efficiency of the InBi-3D-supported Au sample.

Dai and coworkers [65] prepared 3DOM  $\text{BiVO}_4$  (3D-BiV), AgBr/3D-BiV, and  $M/\text{AgBr}/3\text{D-BiV}$  ( $M = \text{Au}$ , Pt, and Pd) photocatalysts using the PMMA-templating, low-temperature deposition, and PVA-protected reduction methods, respectively. The AgBr and noble metals were uniformly distributed on the surface of 3D-BiV. The 3DOM  $\text{BiVO}_4$  sample performed better than the commercial  $\text{TiO}_2$  sample. The 10 wt% AgBr/3D-BiV sample exhibited a reduced performance, which might be caused by the shielding effect of excessive AgBr in visible-light spectrum on the 3DOM  $\text{BiVO}_4$  support. When noble metal was deposited on the surface of 10 wt% AgBr/3D-BiV, the photocatalytic performance was much improved, and the 0.17 wt% Pd/AgBr/3D-BiV sample performed the best: Almost complete degradation of 4-chlorophenol was achieved within 150 min of visible-light illumination. The authors assigned the excellent photocatalytic performance of 0.17 wt% Pd/AgBr/3D-BiV to the good 3DOM structure, high surface oxygen adspecies concentration, easy transfer and separation of photogenerated carriers, and synergistic effect between AgBr or Pd nanoclusters and  $\text{BiVO}_4$ .

## 4. Heteroatom-doped $\text{BiVO}_4$ photocatalysts

Up to now, many investigations have been made to improve the photocatalytic performance of visible-light-responsive  $\text{BiVO}_4$  by doping heteroatoms that can efficiently avoid the charge recombination via trapping both electrons and holes. The co-doping with both cations and anions can also extend the visible-light absorption spectrum of  $\text{BiVO}_4$ .

### 4.1. Doping with anions

Yin et al. [66] reported the one-step fabrication of high-performance C-doped  $\text{BiVO}_4$  photocatalyst with hierarchical structures under visible-light irradiation. The sample calcined at  $400^\circ\text{C}$  with a carbon content of 1.5 wt% showed the best photocatalytic MB degradation efficiency (100% degradation after 1 h of visible-light irradiation), which was 6.3 times higher than that over the pure  $\text{BiVO}_4$  sample (18% degradation after 1 h of visible-light irradiation). The XRD result showed that 1.5 wt% C- $\text{BiVO}_4$  had a smaller crystalline size (18.7 nm) in comparison with pure  $\text{BiVO}_4$  (28.5 nm). Moreover, the bandgap energy of 1.5 wt% C- $\text{BiVO}_4$  was about 2.39 eV, which was smaller than that (2.46 eV) of pure  $\text{BiVO}_4$ . The photocatalytic performance was enhanced by C-doping because it improved the efficient separation and transfer of the photogenerated electrons and holes, as evidenced by the results of electron paramagnetic resonance (EPR) measurements.

Tan et al. [67] fabricated a N-doped monoclinic BiVO<sub>4</sub> photocatalyst via a facile microwave hydrothermal route using NaN<sub>3</sub> as nitrogen source. The photocatalytic performance of the samples was evaluated by the decolorization of RhB under the simulated sunlight irradiation. After 4 h of the simulated sunlight irradiation, the degradation efficiencies over the pure BiVO<sub>4</sub> and N-doped BiVO<sub>4</sub> samples were 48 and 97%, respectively, indicating that N-doped BiVO<sub>4</sub> was twice as active as pure BiVO<sub>4</sub>. The bandgap energy (2.0 eV) of N-doped BiVO<sub>4</sub> was narrower than that (2.2 eV) of pure BiVO<sub>4</sub>, whereas the surface area (1.34 m<sup>2</sup>/g) of the former was close to that (0.21 m<sup>2</sup>/g) of the latter. The enhancement in photocatalytic activity could be attributable to the small particle size, narrow bandgap, and most importantly, the existence of multi-atomic BiVO<sub>4</sub> centers and surface oxygen vacancies, which improved the mobility of charge carriers and inhibited the recombination of charge carriers.

F-doped BiVO<sub>4</sub> particles were synthesized through a simple two-step hydrothermal process [68]. The XRD results demonstrated that the presence of F<sup>-</sup> ions did not change the phase structure of monoclinic BiVO<sub>4</sub>. F-doped BiVO<sub>4</sub> was consisted of relatively uniform spheres with a diameter of 2–4 μm, and the bandgap energy was 2.39 eV. When the BiVO<sub>4</sub>/NaF molar ratio was 1: 0.9, the derived F-doped BiVO<sub>4</sub> sample exhibited the highest photocatalytic MB degradation activity (99% MB was degraded after 3 h of visible-light irradiation). The appropriate amount of F<sup>-</sup> ions introduced into the BiVO<sub>4</sub> crystal lattice might effectively restrain the recombination of photogenerated electron–hole pairs, thus facilitating the improvement in photocatalytic activity.

Jiang et al. [69] prepared fluoride-doped BiVO<sub>4</sub> with the different F/Bi molar ratios using the hydrothermal strategy with the hydrothermally derived BiVO<sub>4</sub> as precursor and NH<sub>4</sub>F as fluoride source. All of the samples were of single-phase monoclinic scheelite structure. The doping of fluorine did not induce any alteration in crystal structure but changed the morphology of the sample particles. Compared to the undoped BiVO<sub>4</sub> sample, the fluoride-doped BiVO<sub>4</sub> samples showed higher oxygen adspecies concentration. When the F/Bi molar ratio was 0.29, the BiVO<sub>4</sub> sample with a surface area of 14.6 m<sup>2</sup>/g and a bandgap energy of 2.42 eV performed the best for the degradation of phenol, giving a 97% phenol degradation efficiency within 2 h of visible-light irradiation. The authors concluded that the excellent photocatalytic performance of fluoride-doped BiVO<sub>4</sub> was associated with its higher surface area and adsorbed oxygen species concentration, stronger optical absorbance performance, and lower bandgap energy.

Other anions (e.g., S and B) were also doped into the BiVO<sub>4</sub> lattice (**Table 3**). For example, Guo et al. [70] found that S-doped BiVO<sub>4</sub> was superior to pure BiVO<sub>4</sub> in photocatalyzing the degradation of MB under visible-light irradiation, since an appropriate amount of S<sup>2-</sup> ions could improve the separation efficiency of photogenerated electron–hole pairs and hinder their recombination.

Photocatalyst	Crystal structure	Crystallite size (nm)	Surface area (m <sup>2</sup> /g)	E <sub>g</sub> (eV)	Reaction condition	Degradation efficiency and light illumination time	References
0.5 wt% C-BiVO <sub>4</sub>	Monoclinic	35.7	1.18	–	Visible light, 200 mL phenol (5 mg/L), 0.2 g sample	88.7% and 5 h	[79]
4 mol% B-BiVO <sub>4</sub>	Monoclinic	23.0	4.17	2.34	Visible light, 50 mL MO (15 mg/L), 0.01 g sample	96% and 50 min	[80]
F-BiVO <sub>4</sub> (F/Bi molar ratio = 0.29)	Monoclinic	–	14.6	2.42	Visible light, 200 mL phenol (0.2 mmol/L), 0.2 g sample	97% and 2 h	[69]
0.17 wt% S-BiVO <sub>4</sub>	Monoclinic	29.01	3.18	2.44	Visible light, 100 mL MB (10 mg/L), 0.1 g sample	100% and 25 min	[70]
0.08 wt% S-BiVO <sub>4</sub>	Monoclinic	–	9.9	2.40	Visible light, 100 mL MB (0.005 mmol/L), 0.01 g sample	95% and 2 h	[71]
1.40 wt% FeO <sub>x</sub> /BiVO <sub>4-δ</sub> S <sub>0.08</sub>	Monoclinic	–	5.1	2.39	Visible light, 100 mL MB (0.01 mmol/L), 0.01 g sample	100% and 90 min	[72]
N-BiVO <sub>4</sub> (N : Bi molar ratio = 0.2)	Monoclinic	49.8	3.03	2.23	Visible light, 50 mL MO (10 mg/L), 0.01 g sample	85% and 50 min	[81]
1% wt% Cu-BiVO <sub>4</sub>	Monoclinic	39.78	15.37	1.90	UV light, 90 mL MB (5096 mg/L), 0.15 g sample	5096% and 2 h	[82]
2 mol% Mo-BiVO <sub>4</sub>	Monoclinic	–	0.1	2.39	Visible light, MB (16 ppm), 0.1 g sample	100% and 1.5 h	[78]
1.08 wt% Er-BiVO <sub>4</sub>	Monoclinic	–	4.39	2.11	Visible light, 100 mL MO (10 mg/L), 0.2 g sample	99.4% and 3 h	[83]
8 mol% Yb-BiVO <sub>4</sub>	Tetragonal	–	11.02	2.9	Sunlight, 50 mL RhB (5 mg/L), 0.05 g sample	98% and 2 h	[84]
3 mol% Yb/0.75 mol % Er-BiVO <sub>4</sub>	Monoclinic/tetragonal	–	4	2.35/2.68	UV-vis-NIR light, 150 mL MB (10 ppm), 1 g/L sample	100% and 1 h	[77]
0.8 wt% Eu/4 wt% B-BiVO <sub>4</sub>	Monoclinic	44.89	4.61	2.28	Visible light, 50 mL MO (15 mg/L), 0.015 g sample	90% and 50 min	[76]

**Table 3.** Physical properties and photocatalytic activities of the heteroatom-doped BiVO<sub>4</sub> photocatalysts.

Employing a dodecylamine-assisted alcohol-hydrothermal method in the absence and presence of thiourea or Na<sub>2</sub>S, Zhao et al. [71] synthesized the sulfur-doped BiVO<sub>4</sub> samples. The S-doped samples possessed a monoclinic scheelite structure and a surface area of 8.4–9.9 m<sup>2</sup>/g, and the bandgap energies of the S-doped BiVO<sub>4</sub> samples were narrower than that of pure BiVO<sub>4</sub>. The S-doped BiVO<sub>4</sub> sample with a S content of 0.78 wt% showed the best photocatalytic performance for the degradation of MB and formaldehyde. The photodegradation efficiency of MB was 92% within 2.5 h of visible-light illumination, but only 45% MB was degraded over pure BiVO<sub>4</sub> under the same conditions. It is believed that a higher adsorbed oxygen species concentration and a lower bandgap energy were responsible for the excellent photocatalytic activity of the 0.78 wt% S-BiVO<sub>4</sub> sample. These authors also investigated the porous olive-like morphological S-doped bismuth vanadate-supported iron oxide ( $y\text{FeO}_x/\text{BiVO}_{4\delta}\text{S}_{0.08}$ ,  $y = 0.06\text{--}1.40$  wt%) photocatalysts derived from the dodecylamine-assisted alcohol-hydrothermal and incipient wetness impregnation methods [72]. It is shown that the  $y\text{FeO}_x/\text{BiVO}_{4\delta}\text{S}_{0.08}$  photocatalysts possessed a monoclinic scheelite BiVO<sub>4</sub> phase, a porous olive-like shape, a surface area of 8.8–9.2 m<sup>2</sup>/g, and a bandgap energy of 2.38–2.42 eV. Bi<sup>5+</sup>, Bi<sup>3+</sup>, V<sup>5+</sup>, V<sup>3+</sup>, Fe<sup>3+</sup>, and Fe<sup>2+</sup> species were concurrently present on the surface of  $y\text{FeO}_x/\text{BiVO}_{4\delta}\text{S}_{0.08}$ . Among all of the as-fabricated samples, the 1.40 wt% FeO<sub>x</sub>/BiVO<sub>4δ</sub>S<sub>0.08</sub> sample showed the highest photocatalytic activity for MB degradation under visible-light irradiation. It is concluded that the sulfur and FeO<sub>x</sub> co-doping, higher adsorbed oxygen species concentration, and lower bandgap energy were responsible for the excellent visible-light-driven catalytic activity of 1.40 wt% FeO<sub>x</sub>/BiVO<sub>4δ</sub>S<sub>0.08</sub>.

## 4.2. Doping with cations

Cation doping is another approach to enhance the photocatalytic degradation efficiency of BiVO<sub>4</sub>, including transition metal doping and rare-earth doping (Table 3). For example, Li et al. [73] prepared Cu-doped monoclinic BiVO<sub>4</sub> by a facile hydrothermal method and used the degradation of RhB to evaluate their photocatalytic activities. 1 wt% Cu-BiVO<sub>4</sub> showed the best degradation performance: 95% of RhB was degraded within 80 min of visible-light irradiation, whereas pure BiVO<sub>4</sub> can only degrade 60% of RhB within the same time. The bandgap energy of 1 wt% Cu-BiVO<sub>4</sub> was 2.55 eV, resulting in the photoabsorption ability of the 1 wt% Cu-BiVO<sub>4</sub> sample slightly stronger than undoped BiVO<sub>4</sub> (bandgap energy = 2.57 eV). The amount of oxygen vacancies increased in the copper-doped samples. Possible factors that significantly enhance photocatalytic performance could be as follows: (i) Cu<sup>2+</sup> substituted partial V<sup>5+</sup> ions with lower oxidation state, generating a certain amount of oxygen vacancies; (ii) the generated oxygen vacancies can capture the electrons to suppress recombination of the photoinduced carriers; and (iii) the photoinduced carriers freely diffuse to the active sites on the surface of the photocatalyst where oxidation of organic species takes place.

Zhou et al. [74] prepared a series of visible-light-sensitive monoclinic Co-BiVO<sub>4</sub> photocatalysts by the heteronuclear complexing method with diethylenetriamine pentaacetic acid (DTPA) as chelating agent. The bandgap was narrowed by doping cobalt. The bandgap energies of the Co-doped BiVO<sub>4</sub> samples at cobalt molar content of 0 and 1–10 wt% were 2.44 and 2.39–2.43 eV, respectively. The photocatalytic activity of Co-BiVO<sub>4</sub> was studied by the

decolorization of MB. The 5 wt% Co-BiVO<sub>4</sub> sample exhibited the highest photocatalytic activity with a 85% of MB removal (65% of MB removal by pure BiVO<sub>4</sub>) within 5 h of visible-light irradiation. There was no significant loss of photocatalytic activity in three successive runs (each lasted for 6 h). Therefore, Co-BiVO<sub>4</sub> was photocatalytically stable and resistant to photocorrosion during the photocatalytic degradation of organic dyes.

Obregón et al. [75] synthesized Er-BiVO<sub>4</sub> by means of a microwave-assisted hydrothermal method and examined the photodegradation of MB under sunlike excitation. The Er-doped BiVO<sub>4</sub> sample showed a mixed phase of monoclinic and tetragonal structures. The optimal MB conversion was achieved over the sample with 0.75 atom% of erbium, over which the complete MB degradation was reached after 40 min of light illumination. The reaction rate obtained over this photocatalyst was 20 times higher than that over the undoped BiVO<sub>4</sub> sample. Two clear absorption edges in the diffuse reflectance spectra of the sample appeared, and the corresponding bandgap energies were ca. 2.4 and 2.8 eV, which were associated with the monoclinic and tetragonal phases, respectively. In order to understand the role of erbium doping in the luminescent properties of the sample, the photoluminescence spectra upon 523 and 655 nm excitations were studied. Upon 655 nm excitation, the up-converted emission of the 0.75 atom% Er-BiVO<sub>4</sub> sample was almost suppressed in the 400–600 nm range. Therefore, the dramatic improvement in photocatalytic activity induced by Er<sup>3+</sup> doping could correlate to a co-operative process involving the electronic and luminescence mechanism. This sensitization mechanism could improve the photon efficiency of the photocatalytic process, and the formation of a monoclinic–tetragonal heterostructure could also be responsible for a more effective charge separation.

Co-doping with two different elements can exhibit better photocatalytic activity than the doping of single element. Wang et al. [76] reported that photodegradation of MO over BiVO<sub>4</sub> doped with B species showed a higher MO degradation rate than the pure BiVO<sub>4</sub> sample under visible-light irradiation. With the doping of europium, the photocatalytic MO degradation rate over Eu–B co-doped BiVO<sub>4</sub> increased with the rise in europium content, and then decreased when the amount of europium was high enough. Co-doping of two different elements can further increase the photocatalytic activity due to the synergistic effects of a number of factors (such as higher specific area, smaller  $E_g$ , and more oxygen vacancies) induced by the co-doping of Eu and B.

Obregón et al. [77] also reported a highly active monoclinic–tetragonal BiVO<sub>4</sub> by doping with Yb<sup>3+</sup> and Er<sup>3+</sup>, which can completely photodegrade MB within 1 h of sunlike excitation. According to the results of structural and morphological characterization, one can deduce that the presence of Yb<sup>3+</sup> and Er<sup>3+</sup> induced the stabilization of the tetragonal phase probably due to its partial incorporation into the BiVO<sub>4</sub> lattice. The improved photocatalytic efficiency was ascribed to two reasons: (i) the doping of lanthanide ions favored the co-existence of a monoclinic-tetragonal heterostructure, and such a structural configuration could optimize the charge separation and (ii) Yb<sup>3+</sup> and Er<sup>3+</sup> luminescence tandem led to a supportive photoluminescence up-conversion process, which could render the energy transfer process from erbium ions to the monoclinic BiVO<sub>4</sub> phase.

It should be noted that not all of the photocatalytic activity enhancement can be ascribed to the higher specific area, small crystallite sizes, smaller  $E_g$ , and more oxygen vacancies of the heteroatom-doped BiVO<sub>4</sub> samples. For example, Yao et al. [78] reported that the doping of Mo ions could significantly enhance the photocatalytic activity of BiVO<sub>4</sub> for MB photodegradation, which was due to its strong acidity on the surface instead of the reasons mentioned above. Moreover, many other researchers also studied the effect of heteroatom-doping on photocatalytic activity of BiVO<sub>4</sub>, as been summarized in Table 3.

## 5. BiVO<sub>4</sub>-based heterojunction photocatalysts

In comparison with single-component photocatalyst, the heterostructure photocatalyst usually exhibits a higher photocatalytic performance for the degradation of various organic contaminants since it can facilitate the effective separation of photoinduced carriers and suppress the recombination of the electron-hole pairs, leaving more charge carriers to form reactive species [85].

Absorption of photons by a semiconductor photocatalyst induces the photogenerated electrons and holes. The photogenerated charge carriers are separated or recombined on the way to the surface reaction sites. The charge separation is a crucial factor determining the light to conversion efficiency [9]. Therefore, much attention has been paid on increasing the charge separation efficiency. Fabrication of a heterojunction structure has been recognized as a useful strategy to avoid charge recombination in a semiconductor catalyst.

### 5.1. Co<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> heterojunction

Co<sub>3</sub>O<sub>4</sub> is a *p*-type semiconductor with interesting electronic and magnetic properties, thus various kinds of Co<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> composite structures have been studied [86]. The enhancement in photocatalytic activity of the Co<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> composite is attributed to the efficient charge transfer and separation between Co<sub>3</sub>O<sub>4</sub> and BiVO<sub>4</sub> driven by the internal electric field or potential difference created by the heterojunction.

Long et al. [86] prepared the Co<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> composite photocatalyst with a *p-n* heterojunction semiconductor structure using the impregnation method. These authors observed that the Co<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> composite sample (0.8 wt% cobalt content) obtained after calcination at 300°C showed a much better photocatalytic activity than pure BiVO<sub>4</sub> for phenol degradation under visible-light irradiation. The decrease of phenol concentration over pure BiVO<sub>4</sub> was only about 6% within 3 h of visible-light irradiation, but phenol concentration dropped by 85% after Co<sub>3</sub>O<sub>4</sub> was loaded on the surface of BiVO<sub>4</sub> under the same conditions. The enhanced activity was attributed to the formation of a *p-n* heterojunction structure and the decrease of recombination of photogenerated hole-electron pairs.

Yu and coworkers [87] also investigated the BiVO<sub>4</sub> decorated with Co<sub>3</sub>O<sub>4</sub>, which showed a much higher photocatalytic activity than pure BiVO<sub>4</sub>. The authors believed that the high crystallinity of BiVO<sub>4</sub> and the formed *p-n* heterojunction of Co<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> improved the

photocatalytic performance. The physical properties and photocatalytic activities of the  $\text{Co}_3\text{O}_4/\text{BiVO}_4$  heterojunction samples reported in the literature are summarized in **Table 4**.

Photocatalyst	Surface area ( $\text{m}^2/\text{g}$ )	$E_g$ (eV)	Reaction condition	Degradation efficiency and light illumination time	References
0.8 wt% $\text{Co}_3\text{O}_4/\text{BiVO}_4$	1.38	–	Visible light, phenol (18 mg/L), 3 g/L sample	96% and 3 h	[86]
3 wt% $\text{Co}_3\text{O}_4/\text{BiVO}_4$	8.03	2.34	Visible light, 80 mL acid orange II (20 mg/L), 0.05 g sample	78% and 5 h	[87]
9 wt% $\text{BiVO}_4/\text{TiO}_2$	107.7	–	Visible light, 80 mL RhB (0.01 mmol/L), 0.08 g sample	79% and 6 h	[119]
8 mol% $\text{BiVO}_4/\text{TiO}_2$	17	2.4	Visible light, 50 mL RhB (1 mmol/L), 0.02 g sample	95% and 2 h	[120]
40 mol% $\text{CeO}_2/\text{BiVO}_4$	–	2.40	Visible light, 100 mL RhB (5 mg/L), 0.15 g sample	73% and 4 h	[121]
40 mol% $\text{CeO}_2/\text{BiVO}_4$	–	2.46	Visible light, 50 mL MB (0.02 mmol/L), 0.05 g sample	80% and 30 min	[89]
30 mol% $\text{BiVO}_4/\text{C}_3\text{N}_4$	4.52	2.45	Visible light, 50 mL RhB (0.01 mmol/L), 0.05 g sample	85% and 5 h	[97]
16.7 mol% $\text{BiVO}_4/\text{C}_3\text{N}_4$	12.99	2.25	Visible light, 100 mL MB (10 mg/L), 0.05 g sample	96% and 1 h	[98]
1 wt% GR/ $\text{BiVO}_4$	10	2.38	Visible light, 100 mL RhB (10 mg/L), 0.02 g sample	94% and 140 min	[122]
3 wt% GR/ $\text{BiVO}_4$	44.2	1.94	Visible light, 100 mL RhB (0.01 mmol/L), 0.6 mmol sample	100% and 10 min	[123]
5 wt% RGO/ $\text{BiVO}_4$	15.73	2.41	Visible light, 50 mL RhB (10 mg/L), 0.1 g sample	89% and 3 h	[100]
3 wt% RGO/ $\text{BiVO}_4$	4.84	2.32	Sunlight, 200 mL RhB (7.5 mg/L), 0.15 g sample	96.5% and 6 h	[124]
50 mol% $\text{Bi}_2\text{WO}_6/\text{BiVO}_4$	2.69	2.08	Visible light, 100 mL RhB (0.01 mmol/L), 0.1 g sample	100% and 0.5 h	[105]
3 wt% $\text{Bi}_2\text{WO}_6/\text{BiVO}_4$	–	2.50	Visible light, 50 mL phenol (10 mg/L), 0.15 g sample	81% and 6 h	[125]
2.5 wt% $\text{Cu}_2\text{O}/\text{BiVO}_4$	–	2.4	Visible light, 50 mL MB (0.02 mmol/L), 0.05 g sample	100% and 75 min	[126]
33 wt% $\text{Cu}_2\text{O}/\text{BiVO}_4$	–	2.45	Visible light, 100 mL phenol (100 mg/L), 0.2 g sample	41% and 6 h	[109]

Photocatalyst	Surface area (m <sup>2</sup> /g)	E <sub>g</sub> (eV)	Reaction condition	Degradation efficiency and light illumination time	References
8 wt% CuO/BiVO <sub>4</sub>	–	2.12	Visible light, 30 mL MO (5 mg/L), 0.03 g sample	90.4% and 3 h	[127]
1 wt% CuO/BiVO <sub>4</sub>	2	2.28	Visible light, 100 mL acid orange 7 (0.05 mmol/L), 0.05 g sample	95% and 3 h	[128]
Bi <sub>2</sub> O <sub>3</sub> /BiVO <sub>4</sub> (Bi/V molar ratio = 1.1)	2.3	2.40	Sunlight, 100 mL MB (0.02 mmol/L), 0.05 g sample	100% and 40 min	[129]
Bi <sub>2</sub> O <sub>3</sub> /BiVO <sub>4</sub>	1.48	2.52	Visible light, 100 mL RhB (0.01 mmol/L), 0.1 g sample	88% and 4 h	[113]
43 mol% BiOBr/BiVO <sub>4</sub>	–	2.38	Visible light, 50 mL MB (10 mg/L), 0.05 g sample	97.2% and 4 h	[130]
13 mol% BiOCl/BiVO <sub>4</sub>	2.80	2.38	Visible light, 100 mL MO (0.0263 mmol/L), 0.1 g sample	85% and 11 h	[118]
15 mol% BiIO <sub>4</sub> /BiVO <sub>4</sub>	–	2.40	Visible light, 50 mL RhB (0.01 mmol/L), 0.05 g sample	75% and 5 h	[131]
MoS <sub>2</sub> /BiVO <sub>4</sub>	–	–	Visible light, 100 mL MB (40 mg/L), 0.1 g sample	95% and 2 h	[132]
80 mol% InVO <sub>4</sub> /BiVO <sub>4</sub>	25.45	2.52	Visible light, 100 mL MB (0.02 mmol/L), 0.1 g sample	87% and 2 h	[133]
16.7 wt% Ag <sub>2</sub> O/BiVO <sub>4</sub>	–	2.06	Visible light, 30 mL MO (5 mg/L), 0.03 g sample	91% and 160 min	[134]
22.47 wt% AgBr/BiVO <sub>4</sub>	–	–	Visible light, 75 mL MB (10 mg/L), 0.075 g sample	83.1% and 2.5 h	[135]
10 mol% Ag <sub>3</sub> PO <sub>4</sub> /BiVO <sub>4</sub>	–	2.46	Visible light, 100 mL MB (10 mg/L), 0.05 g sample	92% and 10 min	[136]

**Table 4.** Physical properties and photocatalytic activities of the BiVO<sub>4</sub>-based heterojunction photocatalysts.

## 5.2. TiO<sub>2</sub>/BiVO<sub>4</sub> heterojunction

As we know, TiO<sub>2</sub> has been widely used in environmental purification, H<sub>2</sub> production, photosynthesis, CO<sub>2</sub> reduction, etc. TiO<sub>2</sub> is cheap, stable, nontoxic, and environmentally friendly, and hence an ideal model for investigations of semiconductor photocatalysts [9]. However, a major drawback of TiO<sub>2</sub> is that only UV in the solar spectrum (about 3–5%) can be utilized to initiate the photocatalytic redox processes.

**Table 4** summarizes the physical properties and photocatalytic activities of the TiO<sub>2</sub>/BiVO<sub>4</sub> heterojunction samples reported in the literature. Xie et al. [88] prepared TiO<sub>2</sub>/BiVO<sub>4</sub> nanocomposites with different molar ratios by impregnating BiVO<sub>4</sub> particles into a TiO<sub>2</sub> sol and after a thermal treatment at 450°C. The phenol degradation efficiency (74% after 1 h of visible-

light illumination) over the  $\text{TiO}_2/\text{BiVO}_4$  nanocomposites was as 4 times as that over pure  $\text{BiVO}_4$ . The results of the transient-state surface photovoltage responses and atmosphere-controlled steady-state surface photovoltage spectra demonstrated that the lifetime of photogenerated charge carriers over the nanosized  $\text{BiVO}_4$  sample could be prolonged by approximately millisecond timescale after a proper molar ratio of nanocrystalline  $\text{TiO}_2$  was coupled. The promoted charge separation was responsible for the unexpected high photocatalytic activity for phenol degradation under visible-light irradiation.

### 5.3. $\text{CeO}_2/\text{BiVO}_4$ heterojunction

Apart from the most commonly used  $\text{TiO}_2$  catalyst, cubic fluorite cerium dioxide ( $\text{CeO}_2$ ), a semiconductor with a bandgap energy similar to that of  $\text{TiO}_2$  [89], shows a promising photocatalytic activity for the degradation of various organic dye pollutants [90].  $\text{CeO}_2$  has been used in the splitting of water for  $\text{H}_2$  evolution and the degradation of phenol or chlorinated phenol under UV irradiation [91, 92]. However, the broad bandgap energy of  $\text{CeO}_2$  limits its applications in visible-light illumination [92]. As we know, the heterojunction structure in composite photocatalysts can dominate photoinduced charges in the direction of transport, distance of separation, and rate of recombination, leading to the efficient separation of photogenerated charges and thus greatly improving the photocatalytic activity of the heterojunction-structured sample. If  $\text{BiVO}_4$  is coupled with  $\text{CeO}_2$  to form a heterojunction structure, it is possible to generate visible-light-driven catalysts that show excellent photocatalytic performance.

Wetchakun et al. [89] prepared the  $\text{BiVO}_4/\text{CeO}_2$  nanocomposites by coupling a homogeneous precipitation method with a hydrothermal process. Photocatalytic activities of the as-prepared samples were examined for the degradation of MB, MO, and a mixture of MB and MO aqueous solutions under visible-light irradiation. The XRD patterns reveal that the  $\text{BiVO}_4/\text{CeO}_2$  nanocomposite was composed of  $\text{BiVO}_4$  and  $\text{CeO}_2$ , and  $\text{BiVO}_4$  in the composite sample was present in two crystalline phases. The sample with a  $\text{BiVO}_4/\text{CeO}_2$  molar ratio of 0.6: 0.4 showed the highest photocatalytic activity (the highest MB degradation of 80% was achieved within 30 min of light irradiation). The absorption of  $\text{BiVO}_4/\text{CeO}_2$  nanocomposites increased in the visible-light region (485–505 nm). Moreover, the low bandgap energy (2.46 eV) of  $\text{BiVO}_4/\text{CeO}_2$  nanocomposites also influenced the dyes degradation.

The physical properties and photocatalytic activities of the  $\text{CeO}_2/\text{BiVO}_4$  heterojunction samples reported in the literature are summarized in **Table 4**.

### 5.4. $\text{g-C}_3\text{N}_4/\text{BiVO}_4$ heterojunction

As a promising photocatalyst candidate for organic pollutant removal, graphite-like carbon nitride ( $\text{g-C}_3\text{N}_4$ ) exhibits a relatively high photocatalytic activity under visible-light illumination due to its rapid separation of photoinduced charge carriers [93, 94]. The very negative CB (−1.13 eV) of  $\text{g-C}_3\text{N}_4$  enables a strong reduction power of electrons ( $\text{e}^-$ ) in the CB. Nevertheless, there are still some shortcomings (e.g., the limited visible-light absorption below 450 nm and the low surface area) for the utilization of  $\text{g-C}_3\text{N}_4$  in photocatalysis [95, 96].

Recently, continuous efforts have been made to improve the photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>. Among these, combining g-C<sub>3</sub>N<sub>4</sub> with other semiconductors to construct heterostructures can effectively promote the separation rate of photoexcited charge carriers [97]. BiVO<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> are selected to construct heterojunction photocatalysts according to the following considerations: (i) both BiVO<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> have been proved to be promising visible-light photocatalysts with desirable chemical stability and (ii) their suitable energy band alignments are beneficial for the separation of light-induced electron-hole pairs in the as-formed heterojunction photocatalysts. More importantly, the g-C<sub>3</sub>N<sub>4</sub>/BiVO<sub>4</sub> heterojunction structures can be easily modified to achieve a controllable coverage of g-C<sub>3</sub>N<sub>4</sub> on BiVO<sub>4</sub> via a thermal annealing process, during which the g-C<sub>3</sub>N<sub>4</sub> phase can be thermally etched by oxidation in air [7, 98].

Li et al. [98] prepared an efficient g-C<sub>3</sub>N<sub>4</sub>/BiVO<sub>4</sub> heterojunction photocatalyst with BiVO<sub>4</sub> networks decorated by discrete g-C<sub>3</sub>N<sub>4</sub> nanoislands for highly efficient photocatalytic degradation of MB. There was the co-existence of BiVO<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub> phase in the composite samples. Among these heterojunction photocatalysts, the g-C<sub>3</sub>N<sub>4</sub>/BiVO<sub>4</sub> heterojunction sample with a g-C<sub>3</sub>N<sub>4</sub>/BiVO<sub>4</sub> ratio of 15: 3 performed the best photocatalytically in the degradation of MB. In this sample, the g-C<sub>3</sub>N<sub>4</sub> phase displayed a discrete nanoisland morphology (5–10 nm in diameter), which was attached tightly to the surface of BiVO<sub>4</sub>. The as-synthesized g-C<sub>3</sub>N<sub>4</sub>/BiVO<sub>4</sub> photocatalyst showed a superior visible-light photocatalytic activity, which was about 4.5 and 6.9 times as high as that over pure BiVO<sub>4</sub> and g-C<sub>3</sub>N<sub>4</sub>, respectively. The enhanced photocatalytic activity can be ascribed to the increased charge separation efficiency, fully exposed reactive sites, and separated redox reaction sites as well as excellent visible-light response in the network composites. The physical properties and photocatalytic activities of the g-C<sub>3</sub>N<sub>4</sub>/BiVO<sub>4</sub> heterojunction samples are summarized in **Table 4**.

### 5.5. rGO/BiVO<sub>4</sub> heterojunction

Reduced graphene oxide (rGO) with excellent electrical conductivity and high carrier mobility has been proved to be an excellent media for electron transfer. The widely accepted mechanism for the enhancement in photocatalytic performance is that chemical bonding between rGO and semiconductor could accelerate the transfer of photogenerated electrons in semiconductor to rGO, thus effectively suppressing the recombination of photogenerated carriers [99]. The rGO/BiVO<sub>4</sub> composites have attracted much attention and significant research progress has been achieved.

Wang et al. [100] fabricated the rGO/BiVO<sub>4</sub> nanocomposite photocatalysts with excellent visible-light photocatalytic activities through electrostatic self-assembly via a simple surface charge modification on amorphous BiVO<sub>4</sub> powders with silane coupling agent. The surface areas of rGO/BiVO<sub>4</sub> and BiVO<sub>4</sub> were 23.57 and 2.62 m<sup>2</sup>/g, respectively, and their corresponding bandgap energies were 2.41 and 2.47 eV. The photocatalytic MB degradation efficiency over rGO/BiVO<sub>4</sub> was 94.1%, whereas that over bare BiVO<sub>4</sub> was just 24.1% after 30 min of visible-light irradiation. The smaller particle size with a high surface area and an increased interfacial interaction in rGO/BiVO<sub>4</sub> gave rise to increased photocatalytic reaction sites, extended

photoresponding range, and enhanced photogenerated charge separation and transportation efficiency.

The physical properties and photocatalytic activities of the rGO/BiVO<sub>4</sub> heterojunction samples reported in the literature are summarized in **Table 4**.

### 5.6. Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> heterojunction

As one of the typical Aurivillius oxides with a layered structure, Bi<sub>2</sub>WO<sub>6</sub> has attracted increasing attention in many research fields due to its excellent intrinsic physicochemical properties [101], including ferroelectric piezoelectricity, pyroelectricity, catalytic activity, non-linear dielectric susceptibility, and luminescence. Besides, Bi<sub>2</sub>WO<sub>6</sub> is a typical *n*-type semiconductor with a direct bandgap energy of 2.8 eV and exhibits good photocatalytic performance in the degradation of organic pollutants and the splitting of water under visible-light irradiation [102]. However, pure Bi<sub>2</sub>WO<sub>6</sub> can only respond to the light with a wavelength of less than 450 nm, which accounts for a small part of solar light [103]. In addition, fast recombination of the photoinduced electron-hole pairs in Bi<sub>2</sub>WO<sub>6</sub> restricts photocatalytic performance considerably [104]. Hence, to extend the range of light absorption and accelerate separation of the photogenerated charge carriers in Bi<sub>2</sub>WO<sub>6</sub>, a semiconductor with a low bandgap energy could be doped with Bi<sub>2</sub>WO<sub>6</sub> to generate a heterojunction architecture [105]. For example, Ju et al. [105] prepared the Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> (C-Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub>) heterojunction photocatalyst via a hydrothermal process and after calcination at 600°C. There were co-presence of monoclinic BiVO<sub>4</sub> and orthorhombic Bi<sub>2</sub>WO<sub>6</sub> phases, and no obvious changes in XRD peak shape and position in the calcined (C-Bi<sub>2</sub>WO<sub>6</sub>, C-BiVO<sub>4</sub>, and C-Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub>) and uncalcined (Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub>) samples. The C-Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> sample possessed a better crystallinity than the uncalcined Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub>. The surface areas of the C-Bi<sub>2</sub>WO<sub>6</sub>, C-BiVO<sub>4</sub>, Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub>, and C-Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> samples were 7.67, 3.62, 20.78, and 2.69 m<sup>2</sup>/g, respectively, indicating that calcination at a high temperature led to a decrease in surface area. The C-Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> sample exhibited a higher photocatalytic activity (RhB degradation efficiency reached 100% within 30 min of visible-light illumination) than the C-Bi<sub>2</sub>WO<sub>6</sub>, C-BiVO<sub>4</sub>, or Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> sample. A high surface area did not give rise to a good photocatalytic activity, suggesting that there were other factors influencing the photocatalytic activity of the sample. The bandgap energies of C-Bi<sub>2</sub>WO<sub>6</sub>, C-BiVO<sub>4</sub>, Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub>, and C-Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> were 2.69, 2.30, 2.18, and 2.08 eV, respectively. The results indicate that the C-Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> photocatalyst had a wider light absorption range and a more suitable bandgap energy. Based on the calculated energy bands and trapping experiment results, the authors proposed that the difference of band potentials in the two semiconductors could induce an inner electric field at the interface between Bi<sub>2</sub>WO<sub>6</sub> and BiVO<sub>4</sub>, resulting in the efficient separation of photoinduced electrons and holes on the *n*-*n* heterojunction and a great reduction in recombination of the photoinduced charge carriers. Therefore, the enhanced photocatalytic activity of C-Bi<sub>2</sub>WO<sub>6</sub>/BiVO<sub>4</sub> could be mainly ascribed to the effective separation of photoinduced electron-hole pairs at the heterojunction interface as well as the wider photoabsorption range and better crystallinity.

### 5.7. Cu<sub>2</sub>O/BiVO<sub>4</sub> heterojunction

Cu<sub>2</sub>O is a *p*-type semiconductor with a direct bandgap energy of 2.0 eV and has a noticeable light absorption capability in the visible-light region [106]. The physical properties and photocatalytic activities of the Cu<sub>2</sub>O/BiVO<sub>4</sub> and CuO/BiVO<sub>4</sub> heterojunction samples reported in the literature are summarized in **Table 4**. For example, Yang et al. [107] reported that the Cu<sub>2</sub>O/TiO<sub>2</sub> network sample showed a much higher photocatalytic activity than the pure TiO<sub>2</sub> sample under the irradiation of artificial solar light, and the enhanced activity of the former could be attributed to the extended absorption in the visible-light region and the effective separation of photogenerated carriers at the *p*-*n* junction interface formed between Cu<sub>2</sub>O and TiO<sub>2</sub>. Since the CB edge of Cu<sub>2</sub>O is much higher than that of BiVO<sub>4</sub> [108], the Cu<sub>2</sub>O/BiVO<sub>4</sub> composite may be an ideal system to form the *p*-*n* junction, consequently enhancing the separation of charge carriers and promoting the photocatalytic activity of BiVO<sub>4</sub>.

Wang et al. [109] prepared the Cu<sub>2</sub>O/BiVO<sub>4</sub> photocatalysts with a heterogeneous nanostructure and a *p*-*n* junction by coupling a hydrothermal process with a polyol strategy. The XRD pattern of the Cu<sub>2</sub>O/BiVO<sub>4</sub> sample was quite similar to that of the pure BiVO<sub>4</sub> nanocrystals, and no obvious peaks due to the Cu<sub>2</sub>O phase were detected. It can be seen from the SEM image of the Cu<sub>2</sub>O/BiVO<sub>4</sub> sample that a large number of Cu<sub>2</sub>O nanoparticles (5–20 nm in size) were assembled on the surface of the BiVO<sub>4</sub> nanocrystals. Under the irradiation of visible light, the photocatalytic phenol degradation efficiency (41.0%) over the Cu<sub>2</sub>O/BiVO<sub>4</sub> sample was more than two times higher than that (20%) of pure BiVO<sub>4</sub> nanocrystals. The bandgap energies of BiVO<sub>4</sub> and Cu<sub>2</sub>O/BiVO<sub>4</sub> were 2.48 and 2.45 eV, respectively. Therefore, the enhanced photocatalytic activity of the Cu<sub>2</sub>O/BiVO<sub>4</sub> sample could be ascribed to formation of the *p*-*n* junction between *p*-type Cu<sub>2</sub>O and *n*-type BiVO<sub>4</sub>. The photogenerated electrons and holes were effectively separated and the recombination of electron-hole pairs was substantially suppressed. Thus, the separated electrons and holes were then free to initiate reactions with the reactants adsorbed on the photocatalyst surface, leading to an enhanced photocatalytic activity.

### 5.8. Bi<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> heterojunction

Bi<sub>2</sub>O<sub>3</sub> is an active *p*-type semiconductor with an  $E_g$  of 2.7–2.8 eV [110]. **Table 4** summarizes the physical properties and photocatalytic activities of the Bi<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> heterojunction samples. Bessekhoud et al. [111] applied the Bi<sub>2</sub>O<sub>3</sub> semiconductor to degrade orange II in water under visible-light illumination. There are few studies in the literature on the use of Bi<sub>2</sub>O<sub>3</sub> as photocatalyst in the degradation of organic dyes [112]. Coupling *m*-BiVO<sub>4</sub> with Bi<sub>2</sub>O<sub>3</sub> to form a heterojunction is an effective approach to enhance the separation of generated electron-hole pairs.

Guan et al. [113] synthesized the BiVO<sub>4</sub> and BiVO<sub>4</sub>@Bi<sub>2</sub>O<sub>3</sub> microspheres with a hollow olive-like morphology and a *n*-*p* core-shell structure by a sodium bis(2-ethylhexyl) sulfosuccinate (AOT)-assisted mixed solvothermal method and a NaOH etching process under hydrothermal conditions. The degradation of RhB was employed to evaluate the photocatalytic activity of the BiVO<sub>4</sub>@Bi<sub>2</sub>O<sub>3</sub> samples. The BiVO<sub>4</sub>@Bi<sub>2</sub>O<sub>3</sub> sample was composed of two phases: monoclinic scheelite BiVO<sub>4</sub> and cubic Bi<sub>2</sub>O<sub>3</sub>. Surface areas of BiVO<sub>4</sub> and BiVO<sub>4</sub>@Bi<sub>2</sub>O<sub>3</sub> were 1.45

and 1.48 m<sup>2</sup>/g, respectively, and their corresponding photocatalytic RhB degradation efficiencies were 42 and 88%. The results indicate that the photocatalytic activity of the sample did not depend on the surface area. The estimated bandgap energies of the BiVO<sub>4</sub> and BiVO<sub>4</sub>@Bi<sub>2</sub>O<sub>3</sub> were 2.43 and 2.52 eV, respectively. In order to probe the reason of enhanced photocatalytic performance, the band-edge positions of the two semiconductors were calculated. The CB-edge potential of Bi<sub>2</sub>O<sub>3</sub> (0.03 eV) was more active than that of BiVO<sub>4</sub> (0.32 eV). Therefore, photoinduced electrons on the surface of Bi<sub>2</sub>O<sub>3</sub> would easily transfer to BiVO<sub>4</sub> under the inducement action of the internal *p-n* electric field, leaving holes on the Bi<sub>2</sub>O<sub>3</sub> VB. In such a way, the photoinduced electrons and holes could be effectively separated. Therefore, the enhanced activity of core-shell BiVO<sub>4</sub>@Bi<sub>2</sub>O<sub>3</sub> microspheres can be mostly attributed to the *p-n* heterojunction structure, thus the reducing the recombination probability of photogenerated hole–electron carriers.

### 5.9. BiOCl/ BiVO<sub>4</sub> heterojunction

In recent years, much attention has been paid on the bismuth oxyhalides (BiOX, X = Cl, Br, I) [114] and their composites in heterogeneous photocatalysis because of their characteristic hierarchical structures and unique optical properties [115]. Among them, BiOCl has drawn considerable attention as a novel photocatalyst due to their unique layered structure and high photocorrosion property [116]. However, BiOCl is similar to TiO<sub>2</sub>, which is semiconductor with a wide bandgap  $E_g$  of 3.5 eV [117] and can only absorb UV light (less than 5% of solar energy), leading to poor photocatalytic activity under visible-light illumination.

A visible-light-active BiOCl/BiVO<sub>4</sub> photocatalyst with a *p-n* heterojunction structure was prepared using a hydrothermal method [118]. There were co-presence of two phases: monoclinic BiVO<sub>4</sub> and tetragonal BiOCl. The highest photocatalytic activity (85% MO was degraded after 11 h of visible-light irradiation) was obtained over the BiOCl/BiVO<sub>4</sub> heterojunction catalyst (BiOCl/BiVO<sub>4</sub> molar ratio = 13: 87). The surface area (2.802 m<sup>2</sup>/g) of this sample was medium in comparison with those of pure BiVO<sub>4</sub> (0.950 m<sup>2</sup>/g), Degussa P25 (56.000 m<sup>2</sup>/g), and other heterojunction catalysts (2.512–5.315 m<sup>2</sup>/g). The absorption edges of pure BiOCl and BiVO<sub>4</sub> were 360 and 520 nm, respectively. The BiOCl/BiVO<sub>4</sub> composites exhibited dual absorption edges at 360 and 520 nm, indicating the co-presence of BiOCl and BiVO<sub>4</sub>. Moreover, the absorbance in the 360–520 nm range gradually decreased with increasing the BiOCl content in the BiOCl/BiVO<sub>4</sub> samples. Because BiOCl had negligible activity for MO degradation under visible-light irradiation, the enhanced photocatalytic activity after addition of BiOCl was due to formation of the heterojunction structure. The physical properties and photocatalytic activities of the BiOX (X = Cl, Br, I)/BiVO<sub>4</sub> heterojunction and other BiVO<sub>4</sub>-based heterojunction samples are listed in **Table 4**.

## 6. Supported BiVO<sub>4</sub> photocatalyst

Due to fast recombination of photogenerated electrons and holes or lack of appropriate reaction sites, single semiconductor-based photocatalysts usually do not show high efficien-

cy in photocatalysis [9]. To improve the photocatalytic performance, it is necessary to fabricate composite photocatalysts by loading proper oxidation or reduction cocatalyst(s) on a semiconductor. In such a composite photocatalyst, the role of the cocatalyst(s) is as follows [9]: (i) providing trapping sites for the photogenerated charges and promoting the charge separation, thus enhancing the quantum efficiency; (ii) improving the photostability of the catalyst by timely consuming the photogenerated electrons and holes; and (iii) catalyzing the reactions by lowering the activation energy. Various kinds of cocatalysts have been applied to BiVO<sub>4</sub> to improve the photocatalytic removal of organics, including metal cocatalysts, metal oxide cocatalysts, and metal sulfide cocatalysts. As early in 2005, Kohtani et al. [137] prepared silver particles loaded on BiVO<sub>4</sub> by an impregnation method for the degradation of 4-*n*-alkylphenols. Since then, noble metal-loaded BiVO<sub>4</sub> has been widely investigated. Because the work function of a noble metal is usually larger than that of most semiconductors, electron transfer from CB of semiconductor to metal happens readily.

Chen et al. [138] prepared the Ag/BiVO<sub>4</sub> composites using a one-step method with ethylene glycol and water as solvent and L-lysine as surfactant. The photocatalytic performance of the composites was evaluated for the degradation of MB in an aqueous solution under visible-light irradiation. Based on the XRD and XPS results, only a small part of the Ag presented as metallic Ag (Ag<sup>0</sup>) dispersed on the surface of BiVO<sub>4</sub>, whereas most of Ag was present in oxidized Ag (Ag<sup>+</sup>). The Ag particles with a size of about 5 nm were in close contact with BiVO<sub>4</sub>. More than 98% of MB could be degraded over 6.5 wt% Ag/BiVO<sub>4</sub> within 100 min of visible-light illumination. The 6.5 wt% Ag/BiVO<sub>4</sub> sample had a surface area of 4.84 m<sup>2</sup>/g and a bandgap energy of 2.4 eV. The results demonstrate that a proper amount of Ag in the composite could promote the separation of photogenerated electrons and holes.

Au/BiVO<sub>4</sub> heterogeneous nanostructures were synthesized using a cysteine-linking strategy through the *in situ* growth of gold nanoparticles on the BiVO<sub>4</sub> microtubes and nanosheets [139]. Many small gold nanoparticles with an average size of 7.2 nm were dispersed on the surface of BiVO<sub>4</sub> microtubes or nanosheets. The bandgap energies of BiVO<sub>4</sub> microtubes, Au-BiVO<sub>4</sub> microtubes, BiVO<sub>4</sub> nanosheets, and Au-BiVO<sub>4</sub> nanosheets were 2.52, 2.51, 2.55, and 2.54 eV, respectively. The MO degradation efficiencies over the Au-BiVO<sub>4</sub> microtubes and nanosheets were 36 and 100% after 50 min of visible-light irradiation, respectively. However, the pure BiVO<sub>4</sub> microtubes and nanosheets exhibited almost no activities for MO degradation. The enhanced photocatalytic efficiency of the Au-loaded sample was attributed to two aspects: (i) the conjugated gold nanoparticles on the BiVO<sub>4</sub> surface might act as electron sinks to retard the recombination of the photogenerated electrons and holes in BiVO<sub>4</sub> so as to improve the charge separation on its surface and (ii) the surface plasmon resonance (SPR) of gold nanoparticles attached on the BiVO<sub>4</sub> surface can also enhance the visible-light photocatalytic efficiency.

**Table 5** summarizes the physical properties and photocatalytic activities of BiVO<sub>4</sub>-supported reduction cocatalysts reported in the literature.

Li et al. [140] prepared the CuO/BiVO<sub>4</sub> photocatalysts by an impregnation method. The highest MB photodegradation efficiency was obtained over the sample with a 5 atom% Cu content and after calcination at 300°C. MB could be completely degraded after 2 h of light irradiation. The

bandgap energies of pure BiVO<sub>4</sub> and 5 atom% CuO/BiVO<sub>4</sub> were 2.40 and 2.34 eV, respectively. Moreover, the surface area (5.62 m<sup>2</sup>/g) of 5 atom% CuO/BiVO<sub>4</sub> was higher than that (1.89 m<sup>2</sup>/g) of pure BiVO<sub>4</sub>. Therefore, the authors concluded that a proper Cu loading could effectively improve the photocatalytic activity.

Photocatalyst	Crystal structure	Crystallite size (nm)	Surface area (m <sup>2</sup> /g)	E <sub>g</sub> (eV)	Reaction condition	Degradation efficiency and light illumination time	References
6.5 wt% Ag/BiVO <sub>4</sub>	Monoclinic	5	4.83	2.40	Visible light, 100 mL MB (0.02 mmol/L), 0.05 g sample	98% and 100 min	[138]
1.5 wt% Ag/BiVO <sub>4</sub>	Monoclinic	10–30	–	2.10	Visible light, MB (10 mg/L), 1 g/L sample	98% and 2 h	[144]
3.5 wt% Au/BiVO <sub>4</sub>	Monoclinic	5	–	2.54	Visible light, 10 mL MO (5 mg/L), 0.01 g sample	100% and 50 min	[139]
1 wt% Au/BiVO <sub>4</sub>	Monoclinic	8–10	–	2.0	Visible light, 50 mL phenol (10 mg/L), 3 g/L sample	99% and 2.5 h	[145]
1 mol% CuO/BiVO <sub>4</sub>	Monoclinic	32.7	5.62	2.34	UV light, 200 mL MB (10 mg/L), 0.2 g sample	100% and 2 h	[140]
5.0 mol% Fe <sub>2</sub> O <sub>3</sub> /BiVO <sub>4</sub>	Monoclinic	20.38	15.27	2.38	Visible light, 50 mL MB (0.05 mmol/L), 0.05 g sample	81% and 0.5 h	[141]
0.1 wt% Pt/0.1 wt% MnO <sub>x</sub> /BiVO <sub>4</sub>	Monoclinic	–	–	–	Visible light, 100 mL MO (10 mg/L), 0.05 g sample	100% and 1.5 h	[142]
0.03 wt% Pt/0.01 wt% RuO <sub>2</sub> /BiVO <sub>4</sub>	Monoclinic	–	–	2.3	Visible light, 30 mL thiophene (600 ppm), 0.05 g sample	78% and 3 h	[143]
1 mol% Ag <sub>2</sub> O/BiVO <sub>4</sub>	Monoclinic	100	2.70	2.31	Visible light, 50 mL ibuprofen (10 mg/L), 0.04 g sample	96% and 4 h	[146]
1 wt% PdO/BiVO <sub>4</sub>	Monoclinic	–	–	1.63	Visible light, 30 mL MO (10 mg/L), 0.2 g sample	100% and 15 h	[147]

**Table 5.** Physical properties and photocatalytic activities of the BiVO<sub>4</sub>-supported photocatalysts.

Chala et al. [141] prepared the pure BiVO<sub>4</sub> and Fe-loaded BiVO<sub>4</sub> samples by a hydrothermal method. Photocatalytic activities of the samples were examined using the degradation of MB under visible-light irradiation. The Fe/BiVO<sub>4</sub> sample with an optimal iron loading of 5.0 mol

% showed the best photodegradation performance (81%) within 30 min of visible-light illumination. The iron loading did not affect the crystal structure of BiVO<sub>4</sub>, and the iron oxides (mainly Fe<sub>2</sub>O<sub>3</sub>) might be loaded merely on the surface of BiVO<sub>4</sub>. The bandgap energies of BiVO<sub>4</sub> and 5.0 mol% Fe/BiVO<sub>4</sub> were 2.51 and 2.38 eV, respectively. Loading with Fe<sub>2</sub>O<sub>3</sub> creates subband states in the bandgap of BiVO<sub>4</sub> which could then be easily excited to produce more electron-hole pairs under visible-light irradiation, hence resulting in higher photocatalytic performance. Surface areas of the pure BiVO<sub>4</sub> and 5.0 mol% Fe/BiVO<sub>4</sub> samples were 6.44 and 15.27 m<sup>2</sup>/g, respectively, indicating that loading of BiVO<sub>4</sub> with iron oxides led to an increase in surface area. The higher surface area could possibly provide more active sites on the catalyst surface, which gave rise to an enhancement in photocatalytic activity. The physical properties and photocatalytic activities of BiVO<sub>4</sub>-supported cocatalysts and dual cocatalysts reported in the literature are summarized in **Table 5**.

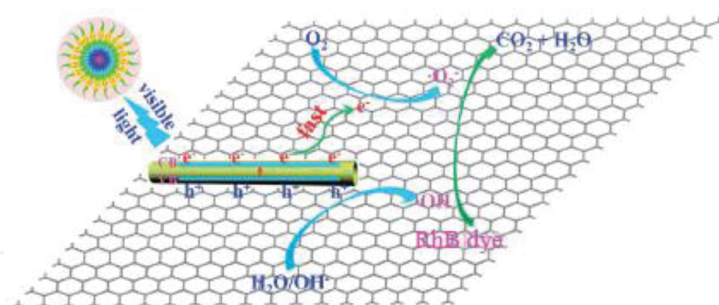
In comparison with single cocatalyst-loaded BiVO<sub>4</sub> photocatalysts stated above, Li et al. [142] prepared two types of photocatalysts (*M*/MnO<sub>x</sub>/BiVO<sub>4</sub> and *M*/Co<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub>, where *M* stands for noble metals) with reduction and oxidation cocatalysts by a photodeposition method for the photocatalytic degradation of MO and RhB. The photocatalytic activity of Pt/MnO<sub>x</sub>/BiVO<sub>4</sub> was remarkably enhanced when Pt and MnO<sub>x</sub> were selectively deposited on the electron-rich and hole-rich facets, which was mainly due to the synergetic effect of dual cocatalysts. Moreover, Lin et al. [143] also studied Pt-RuO<sub>2</sub>/BiVO<sub>4</sub> for photocatalytic oxidation of thiophene under visible-light irradiation. The considerable enhancement in photocatalytic activity also confirmed the simultaneous presence of the reduction and oxidation cocatalysts, which was beneficial for the efficient separation and transfer of the photogenerated electrons and holes.

## 7. Photocatalytic degradation mechanism

### 7.1. Organic dyes photodegradation mechanisms

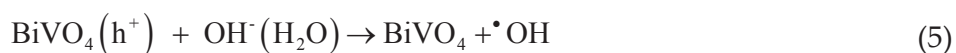
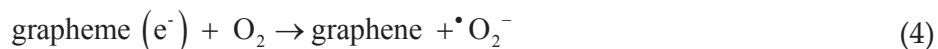
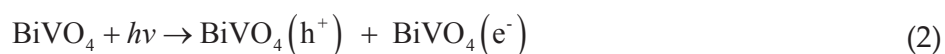
According to the literature, the main factors influencing the degradation rate of organic dyes are hydroxyl radicals ( $\cdot\text{OH}$ ), superoxide radical ( $\cdot\text{O}_2^-$ ), dissolved oxygen (O<sub>2</sub>), and holes (h<sup>+</sup>). The mechanisms for degradation of organic dyes (such as MB, MO, and RhB) are similar. Taking an example, the photocatalytic degradation mechanism over the BiVO<sub>4</sub> quantum tubes-graphene composite sample for the degradation of RhB under visible-light illumination is illustrated in **Figure 11**.

It is well known that a complete photocatalytic process is generally divided into three stages: light harvesting, separation of photogenerated charges, and interfacial reactions [148]. In the photocatalytic reaction of converting dyes to CO<sub>2</sub> and H<sub>2</sub>O over the BiVO<sub>4</sub>-graphene composite material, the electrons (e<sup>-</sup>) are provided by photoexcitation of BiVO<sub>4</sub> (CB electrons). In this regard, BiVO<sub>4</sub> can absorb visible light to generate electron-hole pairs (reaction (1)). In fact, the photogenerated electrons instantly transfer from the CB of BiVO<sub>4</sub> to the carbon atoms of graphene (reaction (2)). Simultaneously, these electrons on the surface of graphene can be captured by the adsorbed O<sub>2</sub> molecules to produce  $\cdot\text{O}_2^-$  (reaction (3)). Meanwhile, the holes on



**Figure 11.** A schematic reaction mechanism illustrating the visible light-driven photodegradation of RhB over the *m*-BiVO<sub>4</sub> quantum tubes-graphene nanocomposite catalyst [123].

the surface of BiVO<sub>4</sub> can be scavenged by the ubiquitous H<sub>2</sub>O molecules or OH<sup>-</sup> to yield •OH radicals (reaction (4)). In this case, the RhB molecules can be subsequently destroyed into CO<sub>2</sub> and H<sub>2</sub>O (reaction (5)) by the generated •O<sub>2</sub><sup>-</sup> and •OH radicals due to their high activities [123].



It is noteworthy that holes (h<sup>+</sup>) can directly react with RhB molecules to generate CO<sub>2</sub> and H<sub>2</sub>O (reaction (6)). Moreover, in order to improve the photocatalytic performance, H<sub>2</sub>O<sub>2</sub> is often added to the dye solution as electronic sacrificial agent. It has been reported that a small amount of H<sub>2</sub>O<sub>2</sub> in the initial dye solution was beneficial for trapping e<sup>-</sup> to form •OH radicals (reaction (7)) and also inhibiting the recombination of e<sup>-</sup>/h<sup>+</sup> pairs.

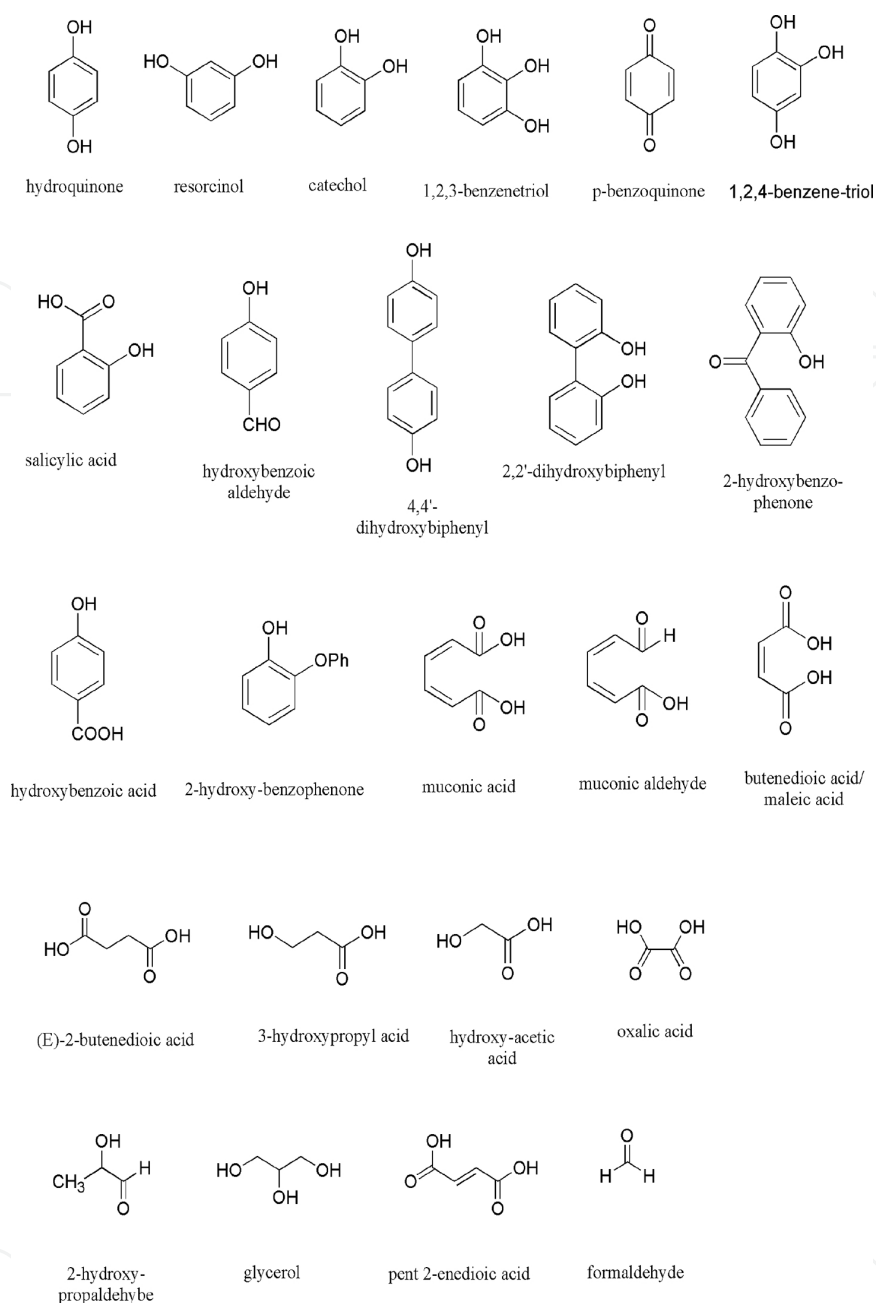
## 7.2. Phenol and its derivatives photodegradation mechanisms

The difference of degradation of phenol and its derivatives from that of degradation of organic dyes is that the intermediate products are usually generated, which are difficult to be completely degraded to CO<sub>2</sub> and H<sub>2</sub>O.



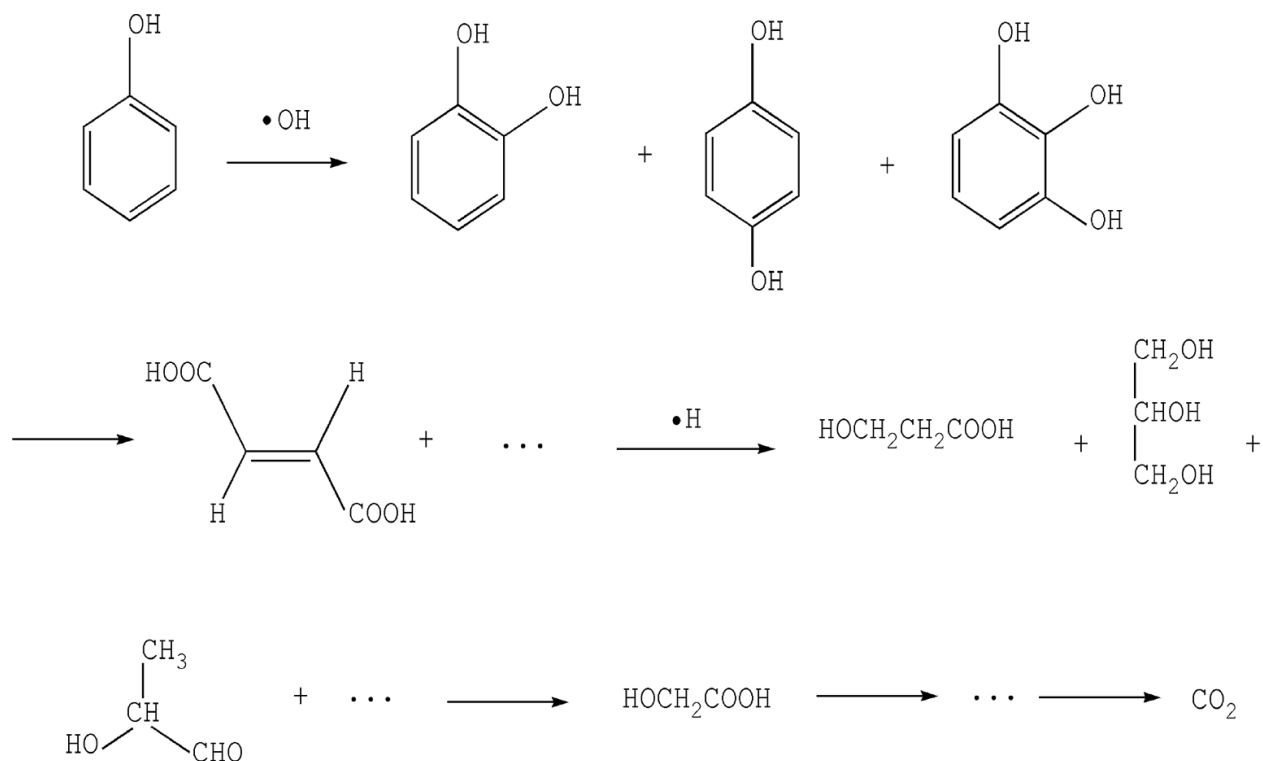
There are at least 20 intermediates (see **Figure 12**) of phenol photodegradation [149], the photodegradation process of phenol is hence very complicated. Furthermore, the routes of phenol photodegradation are different under different experimental conditions. Although the

active species for phenol degradation are also the  $\cdot\text{OH}$ ,  $\cdot\text{O}_2^-$ ,  $\text{O}_2$ , and  $\text{h}^+$ , phenol is difficult to be completely destroyed to CO<sub>2</sub> and H<sub>2</sub>O.



**Figure 12.** Chemical structures of the by-products derived from phenol photocatalytic degradation [149].

For example, Guo et al. [150] studied degradation of phenol ( $C_0 = 100$  mg/L) over  $\text{TiO}_2$  under UV light irradiation. Intermediates were analyzed with gas chromatography/mass spectrometry (GC-MS). The reaction routes were proposed, as shown in **Figure 13**. The  $\cdot\text{OH}$  radicals attack the phenyl ring, yielding catechol, resorcinol, and hydroquinone, then the phenyl rings in these compounds break up to give malonic acid, the formed short-chain organic acids (such as maleic, oxalic, acetic, formic) are finally converted to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .



**Figure 13.** Phenol photodegradation route [150].

Moreover, Devi and Rajashekhar [151] also proposed a possible phenol degradation mechanism over TiO<sub>2</sub> under the conditions of UV light, catalyst dosage = 400 mg/L, phenol concentration = 20 mg/L, and ammonium persulfate (APS) = 100 mg/L, as shown in **Figure 14**.

Based on a plenty of literature, many possible phenol degradation mechanisms have been proposed. Unfortunately and inevitably, the by-products are always generated. It is noted that the toxicity of the by-products generated in phenol degradation processes may be stronger than phenol itself. Therefore, how to directly convert phenol into harmless products is still a big challenge.

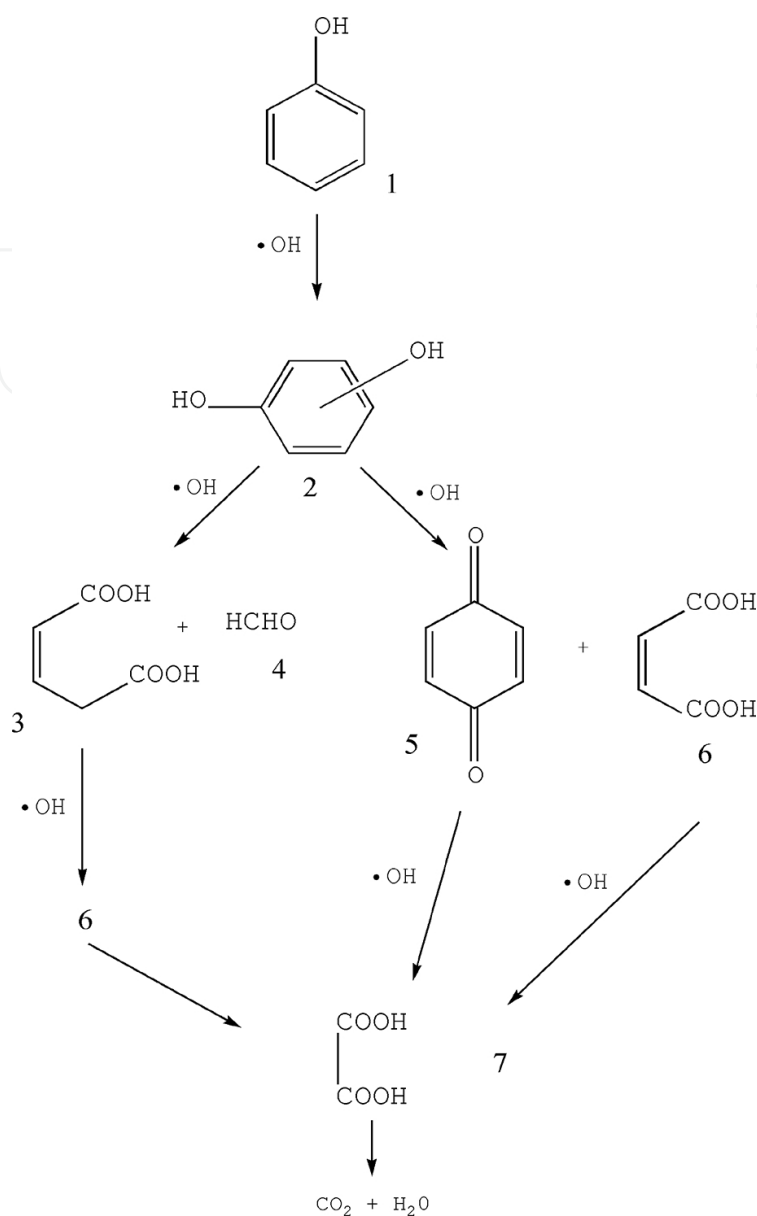


Figure 14. Phenol photodegradation mechanism [151].

## 8. Conclusive remarks and prospect

A large number of  $\text{BiVO}_4$  and its related materials with different morphologies and various structures, such as well-defined morphological  $\text{BiVO}_4$ , porous  $\text{BiVO}_4$ , heteroatom-doped  $\text{BiVO}_4$ ,  $\text{BiVO}_4$ -based heterojunction, and supported  $\text{BiVO}_4$ , have been successfully synthesized in the literature. Most of them show good or even excellent photocatalytic performance for the degradation of organic dyes, phenol or its derivatives under the illumination of visible light. The structure–photocatalytic performance relationship of these materials has been established, and the involved photocatalytic degradation mechanisms have been proposed.

Due to severe situations in water contamination, researchers have devoted themselves to resolve these problems. In particular, the photocatalytic technology has attracted more and more attention because of its unique advantages. However, it has still a long way to make photocatalytic technology widely practicable. Therefore, three strategies are suggested to further improve the photocatalytic performance: (i) It is greatly desired to design and fabricate novel and highly efficient photocatalytic materials; (ii) although photocatalytic reaction mechanisms have been studied for many years, it is still difficult to identify the elementary reaction steps, therefore *in situ* characterization techniques are used to disclose the reaction mechanisms in essence; and (iii) since the photocatalytic performance can be improved significantly if light, heating, plasmon, electric or magnetic field is coupled, the synergetic effects of these energy coupling would be expected to improve the photocatalytic performance of a photocatalyst.

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