Article

# Effect of sulfur doping on the photocatalytic performance of BiVO₄ under visible light illumination

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ABSTRACT

Porous monoclinic bismuth vanadate ($BiVO_{4-\delta}$) and sulfur-doped bismuth vanadates ($BiVO_{4-\delta}S_{0.05}$, $BiVO_{4-\delta}S_{0.08}$, and $BiVO_{4-\delta}S_{0.12}$) were synthesized by a dodecylamine-assisted alcohol-hydrothermal route in the absence and presence of thiourea or $Na_2S$. The physicochemical properties of the materials were characterized and their photocatalytic performance for the degradation of methylene blue and formaldehyde under visible light was evaluated. The samples have a single phase monoclinic scheetlite crystal structure with a porous olive-like morphology, surface areas of 8.4–12.5 $m^2/g$, and bandgap energies of 2.40–2.48 eV. Surface $Bi^{5+}$, $Bi^{3+}$, $V^{5+}$, and $V^{4+}$ species were present on the S-doped $BiVO_{4-\delta}$ samples. Sulfur doping influenced the surface $Bi^{5+}/Bi^{3+}$, $V^{5+}/V^{4+}$, and $O_{ads}/O_{latt}$ molar ratios, and the amount of sulfur doped had an important effect on the photocatalytic performance. Under visible light, $BiVO_{4-\delta}S_{0.08}$ performed the best in the photodegradation of methylene blue and formaldehyde. A higher surface oxygen species concentration and a lower bandgap energy were responsible for the excellent visible light photocatalytic performance of $BiVO_{4-\delta}S_{0.08}$.

## 1. Introduction

Photocatalytic technology is one of the most effective pollution control method. Various kinds of effective and low cost photocatalysts for the degradation of organic pollutants have been investigated. $TiO_2$ has a large bandgap energy (≥ 3.2 eV) and it is only active under UV light, which is only 4% of the solar energy. In recent years, considerable attention has been paid to the synthesis of visible light-responsive photocatalysts. A number of heteroatoms (N, C, S, or F) and metals (La, Fe, or Cr) were used to dope $TiO_2$ to make its bandgap energy narrower (to 2.5–3.0 eV). Meanwhile, Ti-free mixed oxide photo-catalysts, such as $Bi_3NbO_7$ [1] and $Bi_2W_2O_9$ [2], with bandgap energies of 2.0–3.8 eV were reported to have high photocatalytic activity for the degradation of organic materials under visible light illumination. $BiVO_4$ is an effective photocatalyst for the splitting of water [3] and the oxidative degradation of rhodamine B (RhB) [4], methyl orange [5], methylene blue (MB) [6], copper acetylacetonate [7,8], 4-alkylphenols [9], and phenol [5].

It is well known that the catalytic performance of a photocatalyst is related to its surface area, crystal structure, oxygen deficiency, pore structure, crystallite size, and particle morphology. Monoclinic scheelite $BiVO_4$ exhibits a higher photo-

catalytic activity than its tetragonal zircon and tetragonal scheelite counterparts [10,11], which is because it has a lower bandgap energy (2.4 eV) than they do (2.9–3.1 eV). Hierarchical $BiVO_4/Bi_2O_2CO_3$ nanocomposites have shown good photocatalytic performance in the degradation of RhB due to their unique two-dimensional sheet-like morphology, large surface area, and high crystallinity [12]. The doping of a small amount of a heteroatom X (X = F, N, S) into the lattice of a parent metal oxide can result in the narrowing of the band gap by the hybridization of the X 2*p* and O 2*p* orbitals, thus enhancing the absorption of visible light [13]. Furthermore, the generation of oxygen vacancies from X doping can also enhance photocatalytic activity. For example, the formation of oxygen vacancies in $TiO_2$ induced by F- and N-doping is the main factor for the enhancement in visible light-responsive catalytic activity [14]. The doping of $F^-$ into the $SrTiO_3$ lattice narrows its band gap and generates $Ti^{3+}$ and oxygen vacancies, hence promoting electron mobility [15].

Many groups have reported the synthesis and photocatalytic applications of S-doped photocatalysts. For example, S-doped $TiO_2$ exhibited a much higher activity than the N-doped and undoped counterparts [16]. Long et al. [17] found that the S 3*p* orbital is located above the top of the valence band (VB) and it is mixed with the O 2*p* state, thus decreasing the bandgap energy. During their investigation of a S-doped ZnO photocatalyst, Shen et al. [18] observed that the intensity of the UV emission peak decreased with increased S concentration. Li et al. [14] reported that S-doped $In(OH)_3$ was responsive to visible light for the degradation of acetone and dyes. However, there have no reports on the synthesis and photocatalytic applications of S-doped $BiVO_4$ in the literature.

Previously, our group reported the synthesis and physicochemical property characterization of porous and morphological diverse monoclinic $BiVO_4$ samples, such as a porous octapod-like monoclinic $BiVO_4$ for the removal of phenol and MB [19], a porous spherical $BiVO_4$ for the degradation of methyl orange [20], polyhedral, rod-like, leaf-like, and spherical $BiVO_4$ for the degradation of MB [21], three-dimensionally ordered macroporous $BiVO_4$ for the degradation of phenol [22], and flower-, sheet-, and rod-like and spherical $BiVO_4$ for the degradation of methyl orange [23]. In this paper, we report the synthesis and photocatalytic activity of S-doped $BiVO_4$ with a porous olive-like morphology for the degradation of MB and formaldehyde under visible light illumination.

## 2. Experimental

### 2.1. Catalyst preparation

Porous olive-like $BiVO_4$ was prepared by the dodecylamine (DA)-assisted alcohol-hydrothermal method [5] using $Bi(NO_3)_3 \cdot 5H_2O$ and $NH_4VO_3$ as metal source, DA as surfactant, and ethanol and ethylene glycol (EG) as solvent. Concentrated nitric acid (5 ml) and DA (30 mmol) were added to 25 ml of ethanol and EG (volumetric ratio = 1:1) mixed solution. $Bi(NO_3)_3 \cdot 5H_2O$ (10 mmol) and $NH_4VO_3$ (10 mmol) were dissolved in the mixed solution. The pH value was adjusted to 1.5

using NaOH aqueous solution containing absolute ethanol and EG (volumetric ratio = 1:1). The mixture (80 ml) was transferred into a Teflon-lined stainless steel autoclave for alcohol-hydrothermal treatment at 100 °C for 12 h. After washing with deionized water and ethanol and drying at 80 °C overnight, the solid was calcined in air using a ramp of 1 °C/min from room temperature (RT) to 450 °C and kept at this temperature for 4 h, thus obtaining the $BiVO_4$ sample.

The S-doped $BiVO_4$ photocatalysts were synthesized using three methods. One was the DA-assisted alcohol-hydrothermal method. The procedure was the same as for $BiVO_{4-\delta}$ preparation, except that the pH value was adjusted to 1.5 using $Na_2S$ solution containing absolute ethanol and EG (ethanol/EG volumetric ratio = 1:1). The second method was to use uncalcined olive-like $BiVO_4$ soaked in a thiourea aqueous solution (BiVO_4/thiourea molar ratio = 1:2) under stirring and then dried at RT. The material obtained was calcined using a ramp of 1 °C/min in a muffle furnace at 300 °C for 2 h and 450 °C for 3 h. The third method was the same as that of the second one, except that the $BiVO_4$/thiourea molar ratio was 1:4. Inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis indicated that the S content was 1.17, 0.49, and 0.78 wt% for the S-doped $BiVO_4$ samples with $Na_2S$ and thiourea (BiVO_4/thiourea molar ratios of 1:2 and 1:4) as sulfur source, respectively, i.e., the samples were $BiVO_{4-\delta}S_{0.12}$, $BiVO_{4-\delta}S_{0.05}$, and $BiVO_{4-\delta}S_{0.08}$, respectively.

All chemicals (AR) were purchased from Beijing Chemicals Company and used without further purification.

### 2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the $BiVO_4$ and S-doped $BiVO_4$ catalysts were recorded on a Bruker/AXS D8 Advance X-ray diffractometer operated at 40 kV and 35 mA with a Cu $K_\alpha$ X-ray irradiation source ($\lambda$ = 0.15406 nm). The surface areas were determined by $N_2$ adsorption at −196 °C on a Micromeritics ASAP 2020 adsorption analyzer. Before measurement, the catalyst was degassed at 250 °C for 3 h. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Scanning electron microscopy (SEM) was conducted on a Gemini Zeiss Supra 55 apparatus operated at 10 kV. Transmission electron microscope (TEM) images of typical samples were obtained using a JEOL JEM-2010 instrument. X-ray photoelectron spectroscopy (XPS) was used to determine the Bi 4*f*, V 2*p*, O 1*s*, and S 1*s* binding energies (BEs) of surface bismuth, vanadium, oxygen, and sulfur species, respectively, with Mg $K_\alpha$ ($h\nu$ = 1253.6 eV) as the excitation source. Before the XPS measurement, the catalyst was pretreated in an $O_2$ flow of 20 ml/min at 450 °C for 1 h. After cooling to room temperature, the catalyst was transferred to a holder in a Glove Bag (Instruments for Research and Industry, USA) that was filled with He, and then the holder was transferred into the spectrometer chamber under He. Before being analyzed in the analysis chamber, the pretreated catalyst was outgassed in the preparation chamber for 0.5 h. The C 1*s* signal at BE = 284.6 eV was taken as a reference for BE calibration. The chemical composition of the samples was analyzed using X-ray fluorescence

spectroscopy (XRF, Magix PW2403, PANalytical) with a ceramic X-ray tube operated at 3 kW. The sample was finely ground, then placed on a polyethylene plate and compressed into a wafer with a diameter of 3 cm and a thickness of 2–5 mm. The ultraviolet-visible (UV-Vis) diffuse reflectance spectra of the catalysts in the range of 200–800 nm were measured on a Shimadzu UV-2450 UV-Vis spectrophotometer using $BaSO_4$ as the standard.
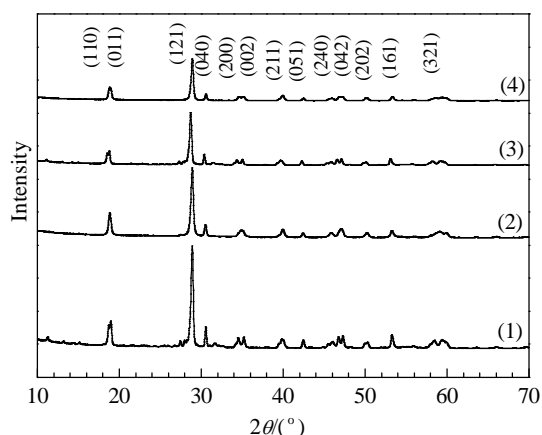
### 2.3. Photocatalytic evaluation

The oxidative degradation of MB and formaldehyde were adopted for the evaluation of the photocatalytic activity of the S-doped $BiVO_4$ samples in a quartz reactor under visible light irradiation using a 300-W Xe lamp with a 400 nm cutoff filter (QO250, Beijing Changtuo Sci. & Technol. Co., Ltd.). The photocatalytic evaluation was conducted at RT as follows. The sample (0.01 g) was suspended in 100 ml of MB-containing aqueous solution (initial MB concentration $C_0$ = 0.005, 0.01, 0.02, 0.03 or 0.04 mmol/L). The sample (0.1 g) was added to 100 ml of a formaldehyde solution (initial formaldehyde concentration $C_0$ = 0.04%). Before illumination, the solution was ultrasonically treated for 10 min and magnetically stirred for 2 h in the dark to ensure adsorption-desorption equilibrium. Then, the suspension was magnetically stirred and exposed to visible light illumination. The temperature of the reaction solution was kept at 25 °C using flowing cool water. The suspension (4 ml) was taken out at 30 min intervals and centrifuged to remove the photocatalyst particles for the analysis of the MB or formaldehyde concentration. The concentration ($C_t$) of MB or formaldehyde in the solution after time ($t$) was monitored by UV-Vis (UV-2010, Shimadzu) and GC (GC-2010, Shimadzu) equipment, respectively. The absorbance of the MB solution at 664 nm during the photodegradation process was determined with the UV-Vis apparatus. $C_t/C_0$ as well as the irradiation times $t_{1/2}$ and $t_{1/10}$ (corresponding to the irradiation time when MB conversion $C_t$ = $(1/2)C_0$ and $(1/10)C_0$, where $C_0$ and $C_t$ are the initial MB concentration and the MB concentration at a given reaction time ($t$), respectively) were used to evaluate the photocatalytic activity of the samples.

## 3. Results and discussion

### 3.1. Crystal phase composition

Figure 1 shows the XRD patterns of the $BiVO_{4-\delta}$ and S-doped $BiVO_{4-\delta}$ samples. All of the diffraction peaks could be indexed to the pure monoclinic scheelite $BiVO_4$ phase (space group: $I2/a$, JCPDS 14-0688) without any impurity phases such as the $Na_2S$, $Bi_2S_3$, or $Na_2SO_3$ phases. The results demonstrated that $S^{2-}$ was homogeneously incorporated into the $BiVO_4$ lattice. Similar XRD patterns of $BiVO_4$ have also been recorded by our group [5] and other researchers [11,24,25]. Some discrepancies in the diffraction intensities of the samples were due to the different preparation procedures adopted. The calcination temperature (450 °C) was appropriate for the complete removal of the surfactant molecules.



**Fig. 1.** XRD patterns of $BiVO_{4-\delta}$ (1), $BiVO_{4-\delta}S_{0.05}$ (2), $BiVO_{4-\delta}S_{0.08}$ (3), and $BiVO_{4-\delta}S_{0.12}$ (4).

### 3.2. Morphology, surface area, and pore size distribution

Representative SEM and TEM images of the $BiVO_{4-\delta}$ and S-doped $BiVO_{4-\delta}$ samples are shown in Fig. 2. The $BiVO_{4-\delta}$ sample displayed a regular olive-like morphology (Fig. 2(a) and (b)) with particle sizes of 1.1–3.0 μm. Macropores (diameter = 82–245 nm) were distributed randomly on the surface similar to those on a porous olive-like $BiVO_4$ [5]. The $BiVO_{4-\delta}S_{0.12}$ sample exhibited a uniform porous olive-like morphology (Fig. 2(j)–(l)) with particle sizes of 0.4–3.0 μm, indicating that the doping of S into the $BiVO_{4-\delta}$ lattice did not influence the particle morphology. The $BiVO_{4-\delta}S_{0.05}$ and $BiVO_{4-\delta}S_{0.08}$ samples were mainly composed of uniform porous olive-like microparticles with particle sizes of 0.5–5.2 μm (Fig. 2(d)–(f) and (g)–(i)), with a small number of particles of irregular morphology. From the high resolution TEM images (Fig. 2(c)) of the $BiVO_{4-\delta}$ sample, one can see that the lattice spacing ($d$ value) of the (121) plane was 0.308 nm, which is close to that (0.31 nm) of the standard monoclinic $BiVO_4$ sample (JCPDS 14-0688). The S-doped $BiVO_{4-\delta}$ samples exhibited two kinds of lattice fringes of the (121) and (040) planes, with $d$ values that were 0.309–0.310 and 0.292–0.293 nm, respectively, which are not much different from those of the standard monoclinic $BiVO_4$ sample.

Figure 3 shows the $N_2$ adsorption isotherms and pore size distribution of the samples. Their BET surface areas are summarized in Table 1. It is observed from Fig. 3(a) that the $N_2$ adsorption-desorption isotherms of these four samples indicated a combination of macroporous and mesoporous structures. The $BiVO_{4-\delta}$ sample exhibited a type II isotherm, while the $BiVO_{4-\delta}S_{0.05}$, $BiVO_{4-\delta}S_{0.08}$, and $BiVO_{4-\delta}S_{0.12}$ samples displayed a type III isotherm. The absence of an adsorption plateau at relative pressures near unity suggested the presence of macropores [26] from the aggregation of nano- or microparticles. The pore size distribution (Fig. 3(b)) of the samples showed one small peak in the range of 2.5–4.5 nm and one broad peak in the range of 10–100 nm, indicating the presence of mesopores and macropores in the samples, which confirmed the TEM observations (Fig. 2(b), (e), (h), and (k)). As can been seen in Table 1, the surface area of the $BiVO_{4-\delta}$ sample was 12.5
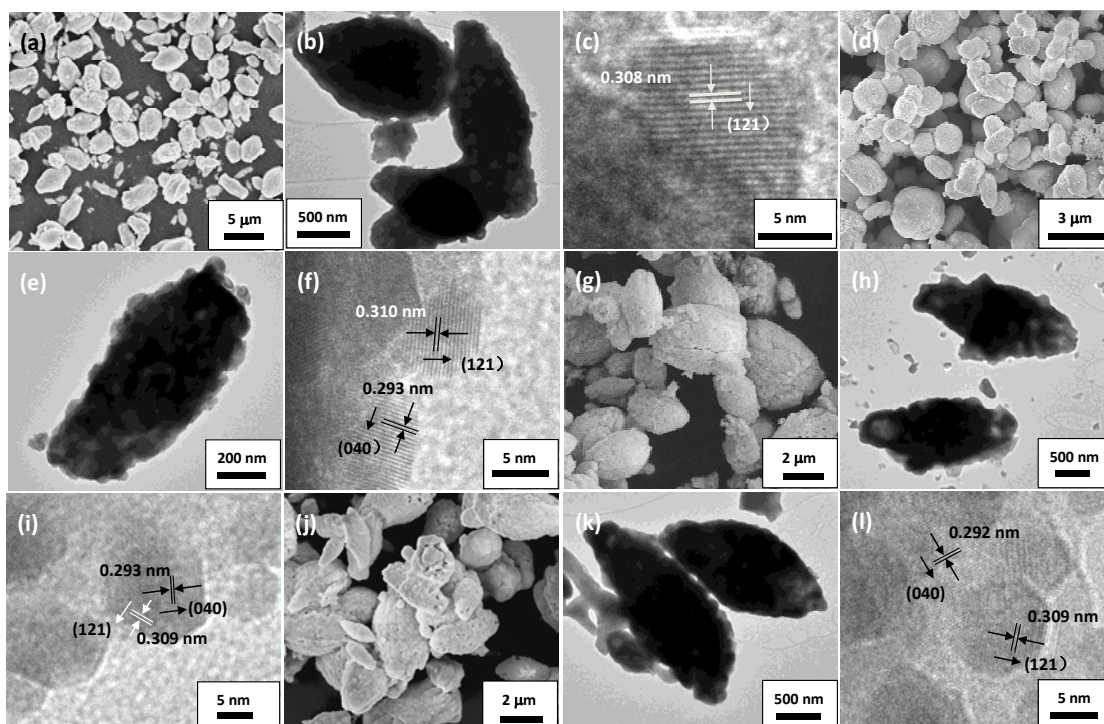
**Fig. 2.** SEM (a, d, g, and j) and TEM (b, c, e, f, h, i, k, and l) images of $BiVO_{4-\delta}$ (a–c), $BiVO_{4-\delta}S_{0.05}$ (d–f), $BiVO_{4-\delta}S_{0.08}$ (g–i), and $BiVO_{4-\delta}S_{0.12}$ (j–l).

$m^2/g$, which is similar to that of the porous olive-like $BiVO_4$ sample previously reported [5]. The surface areas of the S-doped $BiVO_{4-\delta}$ samples were in the range of 8.4–9.9 $m^2/g$, which were lower than that of the undoped sample.



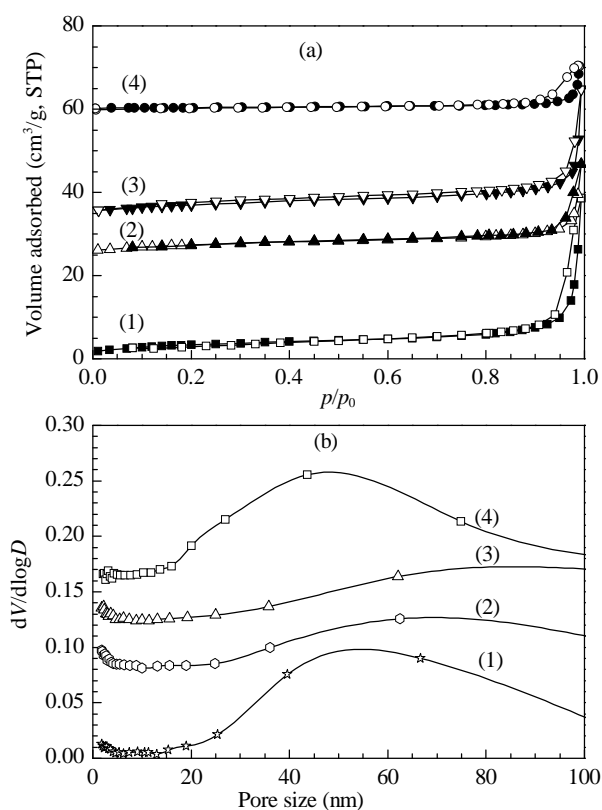**Fig. 3.** $N_2$ adsorption isotherms (a) and pore size distribution (b) of $BiVO_{4-\delta}$ (1), $BiVO_{4-\delta}S_{0.05}$ (2), $BiVO_{4-\delta}S_{0.08}$ (3), and $BiVO_{4-\delta}S_{0.12}$ (4).

### 3.3. Surface composition, metal oxidation state, and oxygen species

The surface composition, metal chemical state, and adsorbed species on the samples were characterized by XPS. Figure 4(a) shows the Bi $4f$ XPS spectra of the samples. Two sets of Bi $4f$ spin-orbit doublet components, Bi $4f_{5/2}$ and Bi $4f_{7/2}$, together with the typical Bi $4f$ spin-orbit splitting of 5.3 eV [27,28], were recorded. For the $BiVO_{4-\delta}$ sample, there were two symmetrical peaks at 158.7 and 164.0 eV, which were assigned to the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ signals of surface $Bi^{3+}$ species [29–31], respectively. The Bi $4f$ spectra of the three S-doped $BiVO_{4-\delta}$ samples could be decomposed into four components at 158.7, 159.8, 164.0, and 165.1 eV. The components at 158.7 and 164.0 eV were attributed to surface $Bi^{3+}$ species, while the ones at 159.8 and 165.1 eV were assigned to surface $Bi^{5+}$ species [32,33]. This showed that there were surface $Bi^{3+}$ species on $BiVO_{4-\delta}$ and surface $Bi^{3+}$ and $Bi^{5+}$ species on $BiVO_{4-\delta}S_{0.05}$, $BiVO_{4-\delta}S_{0.08}$, and $BiVO_{4-\delta}S_{0.12}$. The result indicated that the doping of $S^{2-}$ into the $BiVO_{4-\delta}$ lattice induced a change in the Bi oxida-

**Table 1**
Preparation parameters, crystal phase, BET surface area ($A_{BET}$), and bandgap energy of the $BiVO_{4-\delta}$ and S-doped $BiVO_{4-\delta}$ photocatalysts.

| Photocatalyst | Sulfur source | Crystal phase | $A_{BET}$ ($m^2/g$) | Bandgap energy (eV) |
|---|---|---|---|---|
| $BiVO_{4-\delta}$ | – | monoclinic | 12.5 | 2.48 |
| $BiVO_{4-\delta}S_{0.05}$ | thiourea ($BiVO_4$/thiourea molar ratio = 1:2) | monoclinic | 8.4 | 2.41 |
| $BiVO_{4-\delta}S_{0.08}$ | thiourea ($BiVO_4$/thiourea molar ratio = 1:4) | monoclinic | 9.9 | 2.40 |
| $BiVO_{4-\delta}S_{0.12}$ | $Na_2S$ | monoclinic | 9.4 | 2.43 |

tion state distribution. This effect has also been observed with F- or Cl-doped $Bi_2Sr_2CaCu_2O_8$ [32]. Figure 4(b) shows the V $2p_{3/2}$ XPS spectra of the samples. The asymmetrical V $2p_{3/2}$ signal could be decomposed into two components at 515.9 and 517.6 eV, assigned to surface $V^{4+}$ and $V^{5+}$ species [34–36], respectively. By the electroneutrality principle, we deduced that all of the samples were oxygen-deficient (i.e., $BiVO_{4-\delta}$ or $BiVO_{4-\delta}S_\sigma$) and the surface nonstoichiometric oxygen amount ($\delta$) depended upon the surface $V^{5+}/V^{4+}$ and/or $Bi^{5+}/Bi^{3+}$ molar ratios. This is summarized in Table 2.

In the O 1s XPS spectra of the samples (Fig. 4(c)), the asymmetrical O 1s spectrum could be decomposed into two components at 529.8 and 532.0 eV, which were attributed to surface lattice oxygen ($O_{latt}$) and surface adsorbed oxygen ($O_{ads}$) species [37,38], respectively. The presence of species such as $OH^-$, $CO_3^{2-}$, and physically adsorbed $H_2O$ on the surface was minimized by the pretreatment of the samples before the XPS measurements. Because the BEs of the S 2p signals are between 161 and 162 eV [39,40], which overlapped the BEs (156–167 eV) of the Bi 4f spin-orbit doublet components, we recorded the S 1s spectra of the samples, as shown in Fig. 4(d). For the three S-doped $BiVO_{4-\delta}$ samples, there was only one S 1s signal at 233 eV assigned to surface $S^{2-}$ species. This result indicated that sulfur was successfully incorporated into the $BiVO_{4-\delta}$ lattice. In addition, the signal intensity increased in the sequence of $BiVO_{4-\delta}S_{0.05} < BiVO_{4-\delta}S_{0.08} < BiVO_{4-\delta}S_{0.12}$, implying that more $S^{2-}$ was doped into the $BiVO_{4-\delta}$ lattice than into the $BiVO_{4-\delta}S_{0.12}$ sample.

The surface and bulk compositions of the samples estimated by the quantitative analysis of the XPS and XRF spectra are summarized in Table 2. There was surface Bi enrichment on the $BiVO_{4-\delta}$ and S-doped samples. The surface $Bi^{5+}/Bi^{3+}$ and $O_{ads}/O_{latt}$ molar ratios increased in the sequence of $BiVO_{4-\delta} < BiVO_{4-\delta}S_{0.05} < BiVO_{4-\delta}S_{0.12} < BiVO_{4-\delta}S_{0.08}$. The $BiVO_{4-\delta}S_{0.08}$ sample possessed the highest surface $Bi^{5+}/Bi^{3+}$ (0.26) and $O_{ads}/O_{latt}$ (2.85) molar ratios. The bulk Bi/V molar ratios were close to



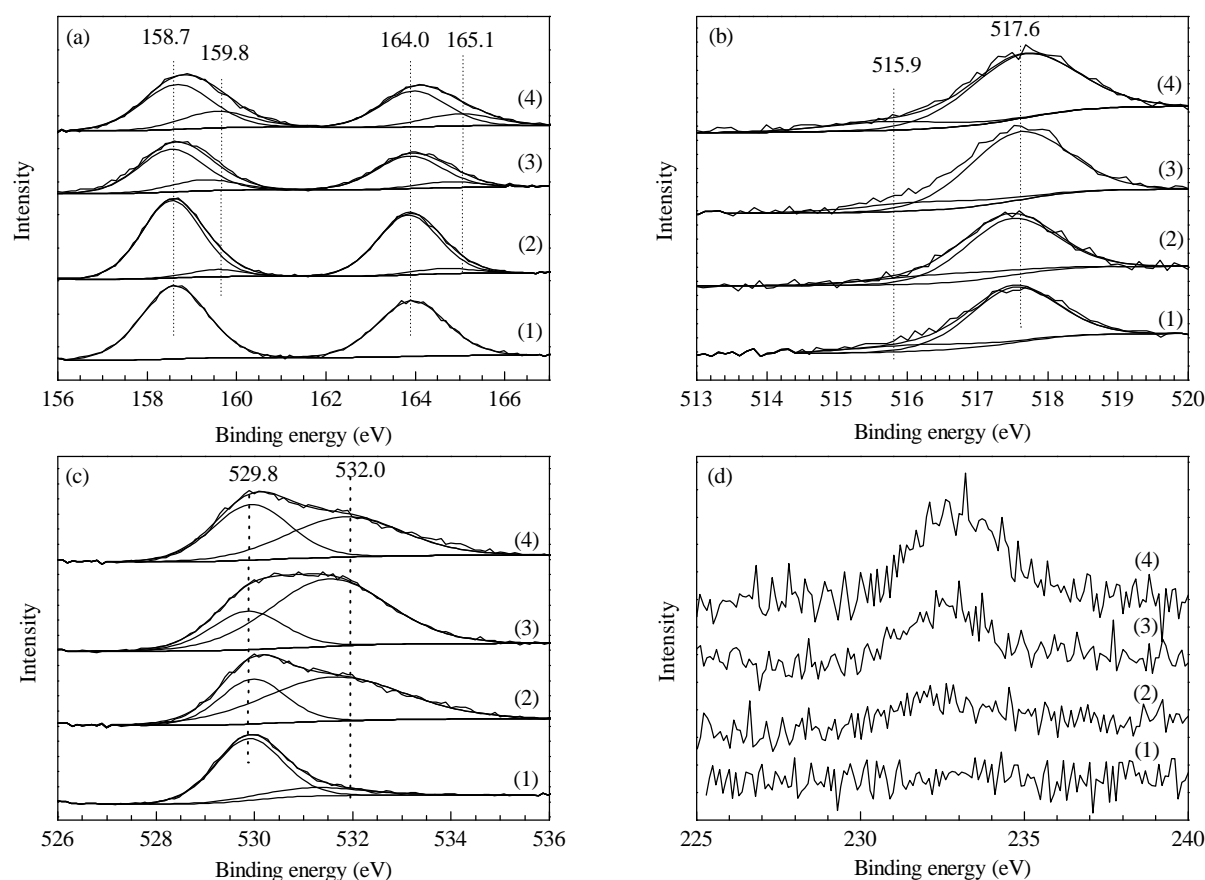**Fig. 4.** Bi 4f (a), V $2p_{3/2}$ (b), O 1s (c), and S 1s (d) XPS spectra of $BiVO_{4-\delta}$ (1), $BiVO_{4-\delta}S_{0.05}$ (2), $BiVO_{4-\delta}S_{0.08}$ (3), and $BiVO_{4-\delta}S_{0.12}$ (4).

**Table 2**
Surface and bulk compositions of the $BiVO_{4-\delta}$ and S-doped $BiVO_{4-\delta}$ photocatalysts.

| Photocatalyst | Surface composition [a] (molar ratio) | | | | | Bulk composition [b] (molar ratio) | |
|---|---|---|---|---|---|---|---|
| | $Bi^{5+}/Bi^{3+}$ | Bi/V | $V^{5+}/V^{4+}$ | $O_{ads}/O_{latt}$ | $S/(O_{ads}+O_{latt})$ | Bi/V | S/O |
| $BiVO_{4-\delta}$ | 0 | 2.94 | 0.16 | 0.21 | 0 | 1.01 | 0 |
| $BiVO_{4-\delta}S_{0.05}$ | 0.08 | 2.27 | 0.22 | 1.96 | 0.010 | 1.01 | 0.011 |
| $BiVO_{4-\delta}S_{0.08}$ | 0.26 | 2.38 | 0.16 | 2.85 | 0.016 | 1.01 | 0.019 |
| $BiVO_{4-\delta}S_{0.12}$ | 0.20 | 2.12 | 0.15 | 1.08 | 0.030 | 1.02 | 0.029 |

[a] Data obtained by XPS; [b] Data obtained by XRF.

1.00, indicating that the $BiVO_{4-\delta}$ and S-doped $BiVO_{4-\delta}$ samples were stoichiometric. The surface $S/(O_{ads}+O_{latt})$ molar ratios of the samples were basically similar to their bulk ratios.

### 3.4. Optical absorption behavior

UV-Vis diffuse reflectance spectroscopy was used to characterize the optical absorption behavior of the samples. Figure 5(a) and (b) show the UV-Vis absorption spectra and optical absorption edges of the $BiVO_{4-\delta}$ and S-doped $BiVO_{4-\delta}$ samples. The samples exhibited strong absorption in the UV and visible light regions, which is a characteristic absorption feature of monoclinic $BiVO_4$ [41,42]. The steep shape of the spectra indicated that the visible light adsorption was due to the bandgap transition from the Bi 6$s$ valence band (VB) to V 3$d$ one [42,43]. We use the formula of $(\alpha h\nu)^2 = A(h\nu - E_g)^n$ to describe the relationship between the absorption coefficient ($\alpha$) and incident photon energy ($h\nu$) [44,45], where $A$ and $E_g$ are a constant and the bandgap energy, respectively. The value of $n$ is 1, which is characteristic of monoclinic $BiVO_4$ [5,46]. The bandgap energies of the $BiVO_{4-\delta}S_{0.05}$, $BiVO_{4-\delta}S_{0.08}$, and $BiVO_{4-\delta}S_{0.12}$ samples were in the range of 2.40–2.43 eV, which were narrower than that (2.48 eV) of the $BiVO_{4-\delta}$ sample. The light absorption ability of the S-doped $BiVO_{4-\delta}$ samples decreased with increased S-doped amount (Fig. 5(a)), in the order of $BiVO_{4-\delta}S_{0.08}$ < $BiVO_{4-\delta}S_{0.05}$ < $BiVO_{4-\delta}S_{0.12}$ < $BiVO_{4-\delta}$, while the bandgap energy

(Fig. 5(b)) became narrower in the same sequence. Hussain et al. [47] also observed that the bandgap energy was reduced with increasing S-doping level. Yang et al. [48] suggested that the S impurity decreased the bandgap energy by the mixing of the Bi 6$s$ VB with S 3$p$. In addition, the mixing states of S 3$s$ and O 2$p$ located in the band gap can result in a reduced photon absorption energy. These results clearly demonstrated that the amount of doped S influenced the light absorbing ability and the bandgap energy.

### 3.5. Photocatalytic degradation of MB

The photocatalytic activity of the samples was evaluated for the degradation of MB and formaldehyde in aqueous solution under visible light illumination. Figure 6(a) presents the photocatalytic performance of the samples. The $t_{1/2}$ and $t_{1/10}$ values are summarized in Table 3. An ultrasonic treatment and stirring process in the dark were adopted to establish adsorption-desorption equilibrium. The MB conversion increased with irradiation time, and the S-doped $BiVO_{4-\delta}$ samples showed a catalytic activity ($t_{1/10}$ = 136–207 min) much higher than that ($t_{1/10}$ = 239 min) of the $BiVO_{4-\delta}$ sample. The $BiVO_{4-\delta}S_{0.08}$ sample performed the best ($t_{1/10}$ = 136 min). Clearly, the photocatalytic performance of the sample improved after sulfur doping. A similar phenomenon was also observed in both phenol degradation and $CO_2$ + $H_2O$ conversion over sulfur-doped $TiO_2$ pho-
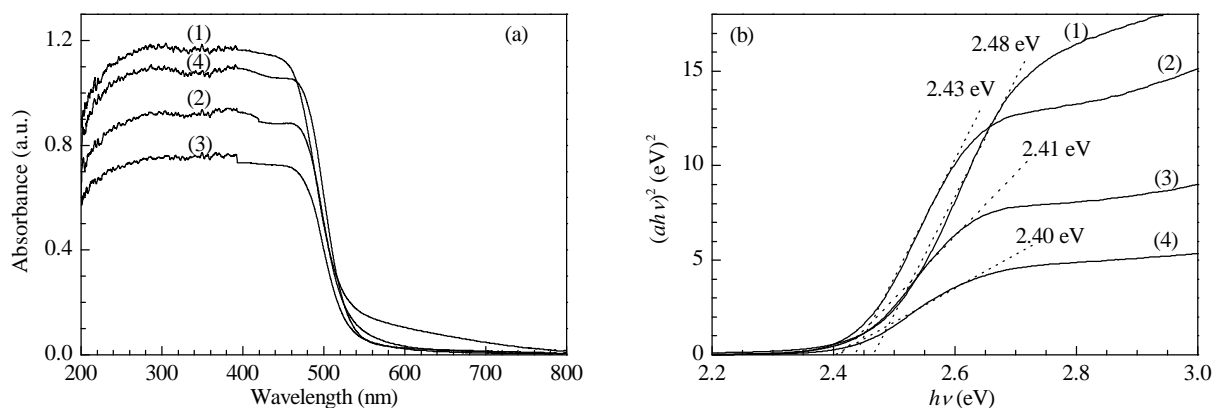


**Fig. 5.** UV-Vis diffuse reflectance spectra (a) and plots of the $(\alpha h\nu)^2$ versus $h\nu$ (b) of $BiVO_{4-\delta}$ (1), $BiVO_{4-\delta}S_{0.05}$ (2), $BiVO_{4-\delta}S_{0.08}$ (3), and $BiVO_{4-\delta}S_{0.12}$ (4).



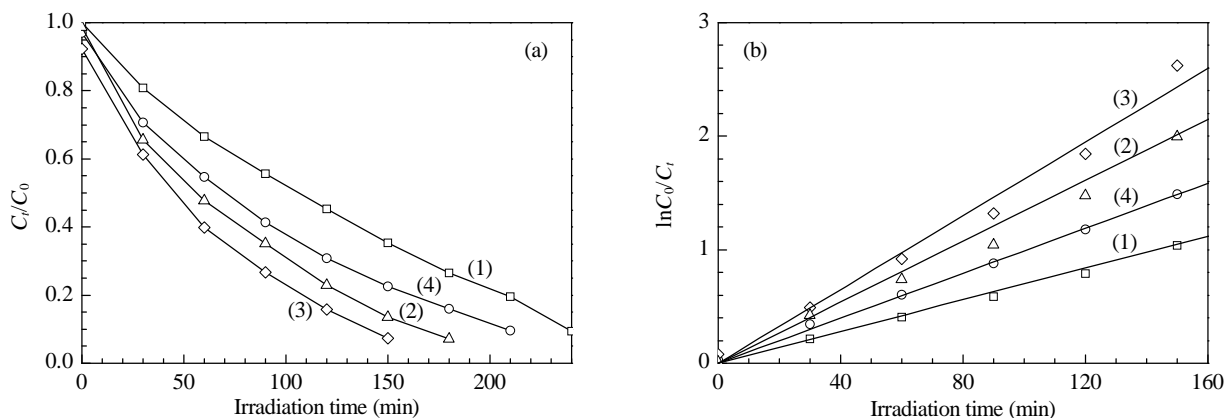**Fig. 6.** Degradation of MB over 0.01 g of $BiVO_{4-\delta}$ (1), $BiVO_{4-\delta}S_{0.05}$ (2), $BiVO_{4-\delta}S_{0.08}$ (3), and $BiVO_{4-\delta}S_{0.12}$ (4) under visible light ($\lambda \geq 400$ nm) illumination. Reaction conditions: $C_0$ = 0.01 mmol/L, temperature = 25 °C, MB solution volume = 100 ml.
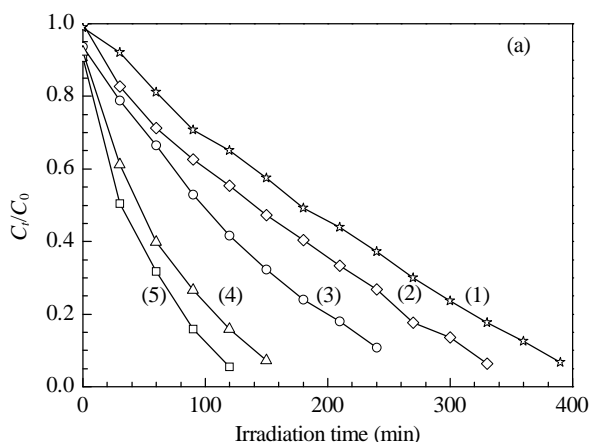
**Table 3**

Correlation coefficients ($R^2$), rate constants ($k$), $t_{1/2}$, and $t_{1/10}$ values of the $BiVO_{4-\delta}$ and S-doped $BiVO_{4-\delta}$ photocatalysts for MB degradation.

| Photocatalyst | $C_0$/(mmol/L) | $R^2$ | $k$/min$^{-1}$ | $t_{1/2}$/min | $t_{1/10}$/min |
|---|---|---|---|---|---|
| $BiVO_{4-\delta}$ | 0.01 | 0.997 | 0.0068 | 105 | 239 |
| $BiVO_{4-\delta}S_{0.05}$ | 0.01 | 0.991 | 0.0128 | 56 | 165 |
| $BiVO_{4-\delta}S_{0.08}$ | 0.01 | 0.983 | 0.0164 | 45 | 136 |
| $BiVO_{4-\delta}S_{0.12}$ | 0.01 | 0.999 | 0.0096 | 71 | 207 |
| $BiVO_{4-\delta}S_{0.08}$ | 0.005 | 0.973 | 0.0226 | 30 | 105 |
| $BiVO_{4-\delta}S_{0.08}$ | 0.02 | 0.991 | 0.0079 | 105 | 260 |
| $BiVO_{4-\delta}S_{0.08}$ | 0.03 | 0.994 | 0.0052 | 136 | 315 |
| $BiVO_{4-\delta}S_{0.08}$ | 0.04 | 0.994 | 0.0041 | 178 | 375 |

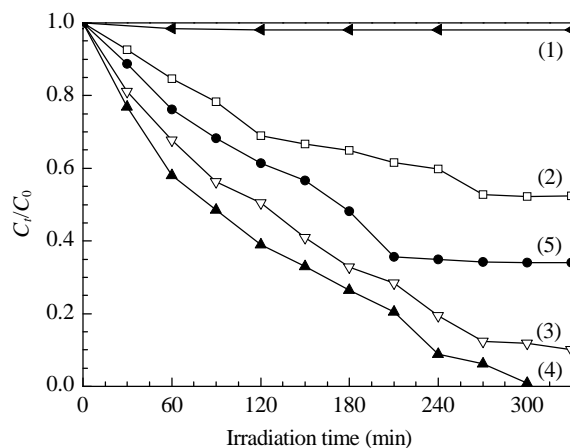tocatalysts under UV and solar irradiation [47,49].

It has been reported that the photocatalytic degradation of MB is a first-order reaction [50,51]. We can express the kinetics with the formula $\ln(C_0/C_t) = kt$, where $k$ is the apparent rate constant. The $k$ values obtained from the slopes of the $\ln(C_0/C_t)$-$t$ lines (Fig. 6(b)) are listed in Table 3. All of the correlation coefficients ($R^2$) were close to 1, indicating a good linear relationship of $\ln(C_0/C_t)$-$t$. The photocatalytic MB degradation rate followed the sequence of $BiVO_{4-\delta}$ (0.0068 min$^{-1}$) < $BiVO_{4-\delta}S_{0.12}$ (0.0096 min$^{-1}$) < $BiVO_{4-\delta}S_{0.05}$ (0.0128 min$^{-1}$) < $BiVO_{4-\delta}S_{0.08}$ (0.0164 min$^{-1}$), which is the order in $O_{ads}$ concentration and the reverse of the order in bandgap energy.

In order to study the effect of initial MB concentrations ($C_0$ = 0.005, 0.01, 0.02, 0.03, and 0.04 mmol/l), we measured the photocatalytic performance of $BiVO_{4-\delta}S_{0.08}$ for the degradation of MB under visible light illumination. The results are shown in Fig. 7. The photodegradation efficiency was enhanced with a decrease in initial MB concentration. This result was similar to that in the photodegradation of 2,4-dichlorophenoxyacetic acid over a Ca-Ce-W-TiO$_2$ composite catalyst under UV light irradiation [52]. With the decrease in initial MB concentration, the slope of the $\ln(C_0/C_t)$-$t$ line became steep, and the reaction rate was faster at a lower concentration (Fig. 7(b)). The $k$ value (0.0052 min$^{-1}$) of the $BiVO_{4-\delta}S_{0.08}$ sample was much higher than that (0.0023 min$^{-1}$) of the $Li_9Fe_3(P_2O_7)_3(PO_4)_2$ sample for the photodegradation of MB in MB aqueous solution (0.03 mmol/L) under visible light illumination [53].



**Fig. 8.** Photocatalytic activities for the degradation of formaldehyde ($C_0$ = 0.04%) in the absence (1) and presence of 0.1 g $BiVO_{4-\delta}$ (2), $BiVO_{4-\delta}S_{0.05}$ (3), $BiVO_{4-\delta}S_{0.08}$ (4), and $BiVO_{4-\delta}S_{0.12}$ (5) under visible light ($\lambda \geq$ 400 nm) illumination. Reaction conditions: temperature = 25 °C, formaldehyde solution volume = 100 ml.

### 3.6. Photocatalytic degradation of formaldehyde

The photocatalytc degradation of formaldehyde over the samples in a 0.04% formaldehyde aqueous solution without the use of electron scavenger (e.g., $H_2O_2$ or $Na_2S$) was examined. For comparison, we also measured the direct photolysis of formaldehyde under visible light illumination. Figure 8 shows the photocatalytic performance of the samples for the degradation of formaldehyde. The formaldehyde concentration was almost unchanged in the direct photolysis process, indicating that the photolysis of formaldehyde was negligible under the adopted conditions. The formaldehyde conversion over the samples after 300 min reaction time increased in the order of $BiVO_{4-\delta}$ (48%) < $BiVO_{4-\delta}S_{0.12}$ (64%) < $BiVO_{4-\delta}S_{0.05}$ (90%) < $BiVO_{4-\delta}S_{0.08}$ (ca. 100%), in good agreement with the sequence of the photocatalytic performance for the degradation of MB. In their study of the photocatalytic decomposition of formaldehyde over a Pt-doped TiO$_2$ catalyst under UV light irradiation, Li et al. [54] observed that formaldehyde was totally decomposed within 80 min. Using $V_2O_5/TiO_2$ as the photocatalyst for
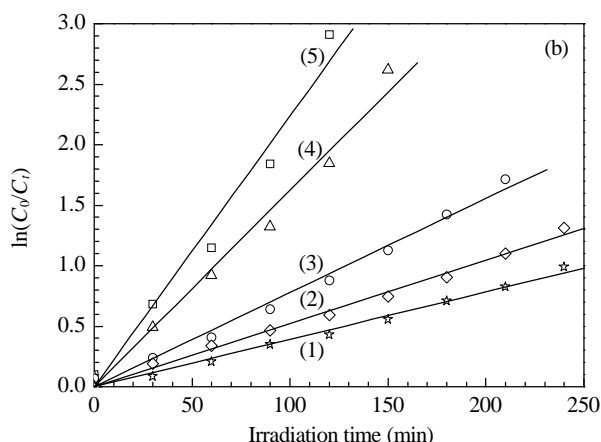


**Fig. 7.** Degradation of MB over 0.01 g of the $BiVO_{4-\delta}S_{0.08}$ sample at initial MB concentration of 0.04 (1), 0.03 (2), 0.02 (3), 0.01 (4), and 0.005 (5) mmol/L under visible-light ($\lambda \geq$ 400 nm) irradiation. Reaction conditions: temperature = 25 °C, MB solution volume = 100 ml.

the degradation of formaldehyde, Akbarzadeh et al. [55] found that the degradation of formaldehyde under sunlight illumination was much better than that under visible or UV light irradiation.

It is generally accepted that photocatalytic performance is influenced by the crystal structure, crystallinity, particle morphology, surface area, oxygen vacancy, pore structure, and bandgap energy [5,56–59]. In the present work, the samples possessed several similar physical properties such as monoclinic scheelite crystal structure, porous architecture, and olive-like particle morphology. Although the $BiVO_{4-\delta}$ sample displayed the highest surface area (12.5 $m^2/g$) and the strongest photon absorbing ability, it showed the worst photocatalytic activity for degradation of MB and formaldehyde. This result means that other factors that are more important determine the photocatalytic performance of the samples, e.g., the bandgap energy and surface oxygen vacancy ($O_{ads}$) concentration. The presence of $Bi^{5+}/Bi^{3+}$ and $V^{5+}/V^{4+}$ couples also contributed to the photocatalytic degradation of pollutants, with the $Bi^{5+}/Bi^{3+}$ and $V^{5+}/V^{4+}$ couples involved in the oxidization or reduction of toxic organic molecules through active species generated by the photo-generated electrons ($e^-$) and holes ($h^+$) on the photocatalyst surface. This reaction would be by the following equations:
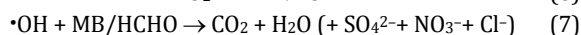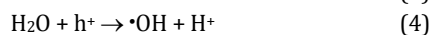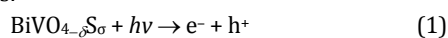
$$BiVO_{4-\delta}S_\sigma + h\nu \rightarrow e^- + h^+ \quad (1)$$
$$Bi^{5+} + 2e^- \rightarrow Bi^{3+} \quad (2)$$
$$V^{5+} + e^- \rightarrow V^{4+} \quad (3)$$
$$H_2O + h^+ \rightarrow {}^\bullet OH + H^+ \quad (4)$$
$$e^- + O_2 \rightarrow O_2^- \quad (5)$$
$$O_2^- + H^+ \rightarrow {}^\bullet OH \quad (6)$$
$${}^\bullet OH + MB/HCHO \rightarrow CO_2 + H_2O\ (+ SO_4^{2-} + NO_3^- + Cl^-) \quad (7)$$

Photo-induced $e^-/h^+$ pairs are generated on the surface of the photocatalyst during irradiation (Eq. (1)). The photo-induced $e^-$ can be easily trapped by $Bi^{5+}$ and $V^{5+}$ ions (Eqs. (2) and (3)), thus effectively reducing the recombination of $e^-/h^+$ pairs. The photo-induced $h^+$ oxidize $H_2O$ molecules adsorbed on the photocatalyst surface into ${}^\bullet OH$ and $H^+$ species (Eq. (4)), while the photo-induced $e^-$ activate $O_2$ molecules adsorbed on the catalyst surface into $O_2^-$ species (Eq. (5)), and $H^+$ reduce the active $O_2^-$ species into ${}^\bullet OH$ species (Eq. (6)). It is known that ${}^\bullet OH$ species are the main active species in the photocatalytic reaction [60,61]. The organic molecules are oxidized by ${}^\bullet OH$ species into inorganic molecules (Eq. (7)). Therefore, we think that active $Bi^{5+}$, $V^{5+}$, and $O_{ads}$ species contribute to the direct or indirect generation of ${}^\bullet OH$ species on the surface of the photocatalyst under visible light illumination, which promoted the photocatalytic degradation of MB and formaldehyde. In other words, doping $S^{2-}$ into the $BiVO_{4-\delta}$ lattice improved photocatalytic activity due to the appearance of $Bi^{5+}$ species and the increased amounts of $V^{5+}$ and $O_{ads}$ species. As shown in Figs. 6–8 and Table 3, the photocatalytic performance was enhanced greatly after the doping of sulfur into the $BiVO_{4-\delta}$ lattice. However, an excessive amount of sulfur doped was not beneficial for the enhancement in photocatalytic activity. Such a phenomenon was also observed by other researchers [49]. Although S-doping induced a decrease in photon absorbing ability, it increased the amount of surface active oxygen species. That is

to say, the doping of sulfur into the $BiVO_{4-\delta}$ lattice gave rise to an increase in $O_{ads}$ concentration, thus enhancing photocatalytic activity. Therefore, it was concluded that the higher $O_{ads}$ concentration and lower bandgap energy were the key factors that accounted for the excellent photocatalytic activity of the $BiVO_{4-\delta}S_{0.08}$ sample.

## 4. Conclusions

Porous $BiVO_{4-\delta}$ and S-doped samples $BiVO_{4-\delta}S_{0.05}$, $BiVO_{4-\delta}S_{0.08}$, and $BiVO_{4-\delta}S_{0.12}$ were prepared using the dodecylamine-assisted alcohol-hydrothermal method in the absence and presence of thiourea or $Na_2S$. All the samples had a single phase monoclinic crystal structure with surface areas of 8.4–12.5 $m^2/g$ and bandgap energies of 2.40–2.48 eV. Surface $Bi^{5+}/Bi^{3+}$ and $V^{5+}/V^{4+}$ couples were present on the S-doped samples. The highest $O_{ads}$ species concentration was that on the $BiVO_{4-\delta}S_{0.08}$ surface. The amount of sulfur doped exerted a crucial effect on the photocatalytic performance of the sample. Under visible light illumination, the $BiVO_{4-\delta}S_{0.08}$ sample showed the best photocatalytic performance for the degradation of methylene blue and formaldehyde. A higher $O_{ads}$ concentration and a lower bandgap energy were responsible for the excellent photocatalytic activity of $BiVO_{4-\delta}S_{0.08}$.

## Acknowledgements

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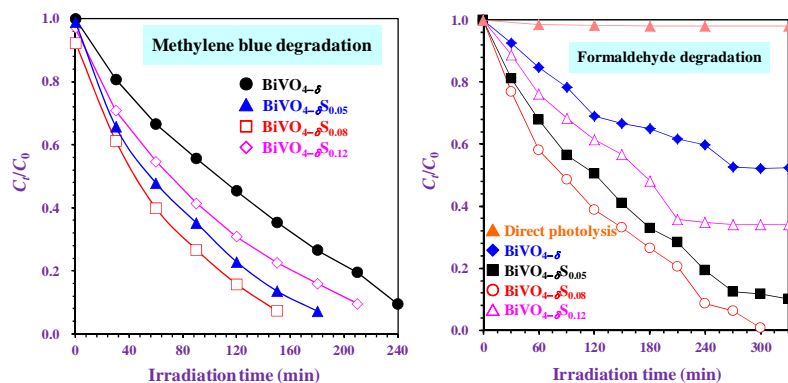[16] Li H X, Zhang X Y, Huo Y N, Zhu J. *Environ Sci Technol*, 2007, 41:

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## Graphical Abstract

**Effect of sulfur doping on the photocatalytic performance of BiVO$_4$ under visible light illumination**

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Porous BiVO$_{4-\delta}$ and BiVO$_{4-\delta}$S$_\sigma$ are fabricated using dodecylamine-assisted alcohol-hydrothermal strategy. The higher O$_{ads}$ concentration and lower bandgap energy account for excellent photocatalytic performance of BiVO$_{4-\delta}$S$_{0.08}$ for methylene blue and formaldehyde degradation.

# 硫掺杂橄榄状BiVO₄上可见光降解亚甲基蓝和甲醛水溶液性能

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**摘要**：在无和有S源(Na₂S或硫脲)存在的条件下，采用十二胺辅助的醇-水热法制备了多孔单斜晶相结构的BiVO₄₋δ和不同含量S掺杂的BiVO₄₋δ光催化剂。利用多种手段表征了催化材料的物化性质，评价了它们在可见光照射下催化降解亚甲基蓝或甲醛的反应活性。结果表明，所制光催化剂为单斜白钨矿晶相结构，具有多孔橄榄状形貌，比表面积为8.4–12.5 m²/g，带隙能为2.40–2.48 eV。在S掺杂BiVO₄₋δ表面同时含有Bi⁵⁺，Bi⁴⁺，V⁵⁺和V⁴⁺物种。S掺杂对BiVO₄₋δ光催化剂的活性影响很大。在可见光下照射下，BiVO₄₋δS₀.₀₈光催化剂对亚甲基蓝和甲醛降解反应显示出最高的光催化活性，这与其较高的表面氧物种浓度和较低的带隙能相关。
**关键词**：硫掺杂；钒酸铋；可见光催化；橄榄状形貌；亚甲基蓝降解；甲醛水溶液降解

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