



Article Enhanced Photocatalytic Performance of Visible-Light-Driven BiVO₄ Nanoparticles through W and Mo Substituting

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Abstract: Bismuth vanadate (BiVO₄), W-doped BiVO₄ (BiVO₄:W), and Mo-doped BiVO₄ (BiVO₄:Mo) nanoparticles were synthesized at pH = 4 using a green hydrothermal method. The effects of 2 at% W or Mo doping on the microstructural and optical characteristics of as-prepared BiVO₄ nanoparticles and the effect of combining particle morphology modification and impurity dopant incorporation on the visible-light-derived photocatalytic degradation of dilute Rhodamine B (RhB) solution are studied. XRD examination revealed that these obtained BiVO₄-based nanoparticles had a highly crystalline and single monoclinic phase. SEM and TEM observations showed that impurity doping could modify the surface morphology, change the particle shape, and reduce the particle diameter to enlarge their specific surface area, increasing the reactive sites of the photocatalytic process. XPS and FL measurements indicated that W- and Mo-doped nanoparticles possessed higher concentrations of oxygen vacancies, which could promote the n-type semiconductor property. It was found that the BiVO₄:W and BiVO₄:Mo powder samples exhibited better photocatalytic activity for efficient RhB removal than that shown by pristine BiVO₄ powder samples under visible light illumination. That feature can be ascribed to the larger surface area and improved concentration of photogenerated charge carriers of the former.

Keywords: BiVO4; impurity doping; nanoparticle; hydrothermal method; photocatalyst; visible-light-driven

1. Introduction

Degradation of harmful substrates, specifically those sourced from industrial wastes, using semiconductor photocatalysts to remove organic pollutants from sewage remains an important issue [1–3]. The photocatalysis degradation approach using functional oxide semiconductors is believed to be an efficient, eco-friendly, and clean strategy for the removal of organic pollutants without any harmful byproduct [4,5]. Past studies have not only involved the selective synthesis of new visible-light-driven photocatalysts, but also focused on the improvement of photocatalytic degradation efficiency for organic contaminants, as well as investigating the effect factors and photocatalytic reaction mechanisms [6–8]. Bismuth vanadate ($BiVO_4$) is a non-titania-based semiconductor photocatalyst and shows promise for application in renewable energy production systems (such as green fuel production from sunlight and water) and the resolution of environmental pollution (such as water remediation and degradation of organic pollutants) [9].

 $BiVO_4$ nanoparticles possess a monoclinic scheelite structure. They are a promising and extensively n-type semiconducting photocatalytic nanomaterial with an optical bandgap energy of approximately 2.4–2.5 eV, and they can be used to harvest solar energy [2,10]. This material has a low production cost, is non-toxic, and possesses considerable chemical stability, as well as exhibiting high photocatalytic activity under visible light irradiation [1]. To improve the photocatalytic activity, it is important to enlarge the specific



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). surface area and improve the density of the photogenerated charge carriers of photocatalysts [7]. Theoretical electronic structural calculations have revealed that both tungsten (W) and molybdenum (Mo) are shallow donors in monoclinic BiVO₄ crystals [11,12]. Substitution of W or Mo ions for some V⁵⁺ sites in BiVO₄ can enhance its n-type characteristics [9,13]. Previous reports have well demonstrated that doping BiVO₄ with W and Mo can extensively improve its photocatalytic performance [14–17]. Thus, appropriate amounts of W or Mo doping could increase the concentration of photogenerated charge carriers and possibly enhance the photocatalytic and photoelectrochemical performance significantly. Parmar and colleagues have reported that BiVO₄ doped with 2 at% W and Mo can dramatically enhance the water photo-oxidation activity [11]. Tian et al. reported that hydrothermal Mo-doped BiVO₄ microcrystals (doping levels of ~2 to 13 mol%) had a better photocurrent density than that of pure BiVO₄ microcrystals [18]. Thalluri et al. found that the optimum surface atomic percentages of dopants for hydrothermally synthesized BiVO₄ powders were 0.9% and 1.2% for W and Mo for sun-derived water oxidation [9].

Several wet-chemical approaches, such as the solution combustion method, sol-gel process, co-precipitation method, and hydrothermal method, can be used for fabricating low-dimensional crystalline oxide nanostructures [8,19]. The hydrothermal synthesis method is convenient and environmentally friendly, and this feasible, low-temperature process allows shape and size control [19]. It is commonly used to prepare $BiVO_4$ -based nanostructures [20]. It is well agreed that variations of the pH value of the hydrothermal reaction solution can strongly affect the morphology, particle diameter, specific surface area, and surface charge of synthesized BiVO₄-based products [8,21]. Dong et al. reported that monoclinic phase BiVO₄ crystalline particles synthesized in acidic solutions (pH < 5) using a hydrothermal method exhibited good adsorption capacity and excellent photocatalytic degradation performance [10]. Li et al. [3] and Ressnig et al. [22] found that $BiVO_4$ nanoparticles synthesized at pH = 4 had excellent photocatalytic activity in organic dye degradation due to the effect of morphological features. In this study, three kinds of $BiVO_4$ -based nanoparticles were synthesized at pH = 4.0 using a hydrothermal method for the photodegradation of Rhodamine B (RhB) solution. Herein, the effects of the impurity dopant (2 at% W or Mo) on the microstructural features and optical properties of as-synthesized BiVO₄ nano-sized products and the improvement of photocatalytic degradation of RhB in aqueous solution through W and Mo doping under visible light illumination at room temperature were investigated.

2. Results and Discussion

2.1. Physical Characteristics of Hydrothermally Synthesized BiVO₄-Based Nanoparticles

Figure 1 presents the XRD patterns of pure BiVO₄, W-doped BiVO₄ (BiVO₄:W), and Mo-doped BiVO₄ (BiVO₄:Mo) powder samples prepared at pH = 4 using a hydrothermal method. The diffraction peaks of the three XRD patterns were identified and in good agreement with the standard data for the monoclinic scheelite BiVO₄ (JCPDS file No. 14-0668); in addition, no diffraction peaks other than those of the mBiVO₄ phase, such as Bi₂O₃, appeared in the XRD patterns of these powder samples. These results indicated that pure monoclinic phase BiVO₄ crystals were obtained. The two theta (2 θ) angular positions of the three relative intensity peaks at 18.88°, 28.83°, and 30.55° identified the (011), (-121), and (040) lattice planes. In addition, sharp diffraction peaks were observed from the three BiVO₄-based samples, revealing that the synthesized oxide powders had good crystallinity.



Figure 1. XRD patterns of BiVO₄, W-doped BiVO₄ (BiVO₄:W), and Mo-doped (BiVO₄:Mo) nanoparticles synthesized using a hydrothermal method at pH 4.0.

These hydrothermally synthesized oxide powders had a monoclinic structure and exhibited preferential growth along the (-121) plane. It is worth noting that the relative intensities of the diffraction peaks of $I_{(011)}/I_{(-121)}$ and $I_{(040)}/I_{(-121)}$ for the BiVO₄:W and BiVO₄:Mo powder samples were 32% to 28% lower than those of the BiVO₄ powder sample $(I_{(011)}/I_{(-121)} = 0.356$ and $I_{(040)}/I_{(-121)} = 0.304$), indicating that the substitution of W and Mo into mBiVO₄ lattices led to enhancement of the growth rate of the (-121) plane and may have caused changes in the particle morphology and diameter. In addition, we also found that the 2 θ angles of the four major diffraction peaks, including (011), (-121), (040), and (161), slightly shifted toward the high 2 θ angle side when BiVO₄ was doped with W or Mo, implying the incorporation of W and Mo ions into mBiVO₄ crystals.

Figure S1 shows three SEM micrographs of the hydrothermally synthesized BiVO₄based nanoparticles. It was found that W or Mo doping significantly influenced the powder morphology. As shown in Figure S1a, both irregular granular and plate-like small particles clustered into micro-sized aggregates. When BiVO₄ was doped with W, the morphology of the as-synthesized powder sample observably changed to aggregates of nano-sized crystals along with acicular-like and slice-like particles (seen in Figure S1b). For the BiVO₄ doped with Mo, ultra-fine aggregated particles were found, as shown in Figure S1c. The measured specific surface areas of the three obtained oxide powder samples are listed in Table 1. The impurity-doped BiVO₄ powder samples exhibited a higher specific surface area (>7.07 m²g⁻¹) than that of the undoped BiVO₄ powder sample (~4.71 m²g⁻¹), and the BiVO₄:Mo powder sample (8.21 m²g⁻¹) had the highest specific surface area. The increased surface area of oxide nanoparticles could provide more active reactive sites during the photocatalytic degradation process [6].

Table 1. Microstructural features, optical characteristics, and photocatalytic activities of hydrothermally synthesized undoped and impurity-doped BiVO₄ nanoparticles.

Photo- Catalyst	Average Particle Size (nm)	$\frac{S_{BET}}{(m^2g^{-1})}$	Main Raman Peak Wavenumber (cm ⁻¹)	Optical Bandgap (eV)	Photo-Degradation Efficiency (%)	Reaction Rate Constant (min ⁻¹)
BiVO ₄	164	4.709	824.4	2.48	61.8	0.0076
BiVO ₄ :W	137	7.079	816.4	2.49	74.4	0.0111
BiVO ₄ :Mo	135	8.214	818.1	2.50	86.8	0.0167

¹ Specific surface area of powder sample.

TEM micrographs of the three BiVO₄-based powder samples are presented in Figure 2, showing the significantly granular morphology of the nanoparticles. The particle size of the sampled nanoparticles was estimated from the corresponding TEM images in ImageJ software, and the average particle sizes of the undoped, W-doped, and Mo-doped BiVO₄ powder samples were determined to be 164, 137, and 135 nm, respectively (Table 1). Iwase et al. have reported that 1 mol% Mo- or W-doped BiVO₄ particles prepared by an aqueous route possessed finer crystallinity than un-doped BiVO₄ [16]. It was recognized that the as-synthesized BiVO₄-based powders comprised nano-sized crystallites, and the average particle sizes of the two impurity-doped samples were finer than that of the undoped sample because the extrinsic doping caused lattice distortion and caused weak internal stress, which apparently led to inhibition of the crystal growth and thus reduced the growth rate.



Figure 2. TEM micrographs of hydrothermally synthesized BiVO₄-based nanoparticles. (**a**) undoped, (**b**) W-doped, and (**c**) Mo-doped BiVO₄ samples.

The presence of the constituent elements of Bi, V, and O in these as-synthesized BiVO₄based nanoparticles, as well as the W and Mo in the two impurity-doped powder samples, were confirmed by wide-scan XPS analysis (data not shown). The core-level XPS spectra of the three BiVO₄-based powder samples taken at the Bi 4f, V 2p, and O 1s binding energy regions are shown in Figure 3. In addition, the W 4f and Mo 3d core-level XPS spectra of the BiVO₄:W and BiVO₄:Mo samples are provided in the Supplementary Materials (Figure S2). The fine-scan XPS examination both identified the chemical bonding states of the elements in these oxide powder samples and confirmed that the Bi 4f, V 2p, W 4f, and Mo 3d orbitals split into two characteristic peaks owing to the spin–orbit interaction, which was consistent with the XPS results of previous reports [11].

In the Bi 4f XPS spectra shown in Figure 3a, the two characteristic peaks located at binding energies of 158.6 eV and 163.8 eV corresponded to the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ states, respectively, indicating that the oxidation state of Bi ions was +3 in the obtained oxide powders [13,23]. A strong V $2p_{3/2}$ peak and a weak V $2p_{1/2}$ peak were located at binding energies of approximately 516.2 eV and 523.8 eV (Figure 3b), representing the oxidation state of V ions of +5 [13,23]. Moreover, it was found that the characteristic peaks of Bi $4f_{7/2}$ and V $2p_{3/2}$ of the W- and Mo-doped BiVO₄ samples slightly shifted toward the low binding energy region due to the impurity doping effect. As shown in Figure S2, the peaks of the W 4f XPS spectrum positioned at 34.9 eV and 36.9 eV were assigned to the W $4f_{7/2}$ and W $4f_{5/2}$ states (Figure S2a), and the characteristic peaks located at 231.9 eV and 235.1 eV exhibited in the Mo 2d XPS spectrum were consistent with the Mo $2d_{5/2}$ and Mo $2d_{3/2}$ states (Figure S2b) [11].



Figure 3. Core-level XPS spectra of (**a**) Bi 4f, (**b**) V 2p, and (**c**) O 1s regions of three BiVO₄-based powder samples.

The O 1s XPS spectra are shown in Figure 3c. Each XPS characteristic curve was divided into two distinct sub-peaks, which were located at 529.4 eV and 530.8 eV for the undoped powder sample. They corresponded to lattice oxygen in mBiVO₄ crystals (O_L) and surface oxygen vacancies (O_v). The area ratios of O_v to O_L sub-peaks for the BiVO₄, BiVO₄:W, and BiVO₄:Mo powder samples were 0.197, 0.222, and 0.255, respectively. These calculated results revealed significant increases in the oxygen vacancy concentrations of the two impurity-doped powder samples. The O_v formation in oxide semiconductors could promote the generation of shallow donors, enhance the absorption of visible light, and improve the photocatalytic activity [24,25]. Moreover, the binding energies of the O_L and O_v sub-peaks of the W- and Mo-doped powder samples showed slight shifts of 0.2 eV toward the lower binding energy side; these were related to changes in the strength of the metal–oxygen bond energy resulting from the substitution of W and Mo ions for V ion sites in BiVO₄ nanocrystals.

Electron spin resonance (ESR) measurement explores the energy absorption behavior of asymmetric electron orbitals under variations in the magnetic field and specific electromagnetic wave frequency. Figure 4 shows three ESR spectra obtained from the undoped and impurity-doped powder samples, revealing significant anisotropy owing to the nature of the crystal-field asymmetry [26]. It was found that the resonance field (Hr = 3384 Oe) and resonance linewidth (Δ H = 300 Oe) of the BiVO₄:Mo sample were higher than those of the BiVO₄ and BiVO₄:W samples (Hr ~ 3372 Oe and Δ H \leq 1000 Oe), indicating that the former possessed a higher magnitude of lattice distortion. The calculated results of the Landé

g-factor for BiVO₄, BiVO₄:W, and BiVO₄:Mo were 2.082, 2.083, and 2.074, respectively. The g-factor of the BiVO₄:Mo sample was close to the g-factor values (2.00) in published reports [16].



Figure 4. ESR spectra of undoped and impurity-doped BiVO₄ powder samples.

The chemical structures of the BiVO₄-based nanoparticles were identified by the Raman analytical technique, and three Raman spectra are presented in Figure 5. The intense band centered at 824.4 cm^{-1} correlated with the symmetric V-O stretching mode (v_s) , and a weak signal located at the low wavenumber side shoulder (713.1 cm⁻¹) was assigned to the anti-symmetric V-O stretching mode (v_{as}) for the pristine crystalline BiVO₄ particles [27]. The spectra related to the symmetric and anti-symmetric bending modes (δ_s and δ_{as}) of the vanadate anion (VO₄³⁻) were found at 363.4 cm⁻¹ and 321.3 cm⁻¹, respectively. In addition, two external modes attributed to rotation and translation were detected at 207.0 cm⁻¹ and 121.7 cm⁻¹, individually. It is well known that the Raman band position, namely the peak wavenumber of the Raman band, is strongly related to the short-range order, and also that the width of the Raman band, namely the full width at half maximum (FWHM), is sensitive to lattice defects and structural disorder, crystallinity, and particle size [8]. The peak position of the most intensive Raman band of the two impuritydoped powder samples shifted toward the low wavenumber side as compared with that of the un-doped powder sample (Figure 5 and Table 1), indicating that the short-range symmetric stretching mode of the VO_4 tetrahedra in the structure of monoclinic BiVO₄ turned into a more regular state [28]. The FWHMs of the most intensive Raman bands for the BiVO₄, BiVO₄:W, and BiVO₄:Mo powder samples were 44.07, 48.37, and 48.87, respectively. That feature revealed that the value of FWHM significantly increased when a small amount of impurity dopant was incorporated into the BiVO₄ crystals and caused slight lattice distortion.

The fluorescence (FL) spectra of the three powder samples were obtained to characterize and explore the recombination rate of photogenerated electrons and holes [29]. As shown in Figure 6, the emission spectra exhibited a strong emission intensity at approximately 514–518 nm when excited by the near-UV light wavelength of 350 nm. The BiVO₄:W and BiVO₄:Mo powder samples had relatively lower emission intensities (spectra (ii) and (iii)), whereas the pristine BiVO₄ powder sample possessed the strongest emission intensity (spectrum (i)). It is well agreed that a stronger FL emission intensity contributes to a higher recombination rate of photogenerated carriers [30]. Therefore, a lower FL intensity implies higher photogenerated electron–hole pair separation efficiency and thus higher photocatalytic activity [31].



Figure 5. Raman spectra of undoped and impurity-doped BiVO₄ powder samples.



Figure 6. Room temperature FL spectra of undoped and impurity-doped BiVO₄ powder samples.

The BiVO₄-based powder samples exhibited similar absorption spectra in the wavelength range of 300–800 nm, as shown in Figure 7a. Each absorption curve showed low absorption in the wavelength range of 600–800 nm; displayed a steep shape absorption feature, representing the absorption edge, within the range of 450–520 nm; and showed a strong absorption ability in the measured wavelength region shorter than 450 nm. The nature of the absorption edge is attributed to the band-to-band transition of direct bandgap semiconductor materials, whereas the absorption bands contained a slight tail extending to the right-sides until approximately 550 nm. This feature resulted from defects in the BiVO₄-based crystals. In addition, it was found that the absorbance magnitudes of the impurity-doped powder samples (curves (ii) and (iii)) were twice as high as that of the un-doped powder sample (curve (i)) in the 600–800 nm region due to the former exhibiting an irregular particle morphology and possessing a much larger specific surface area.

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Figure 7. (a) UV-visible absorption spectra and (b) Tauc plots of three BiVO₄-based powder samples.

Figure 7b depicts the curves of absorption energy (α hv) versus photon energy (hv), which were transferred from the recorded absorbance data. It was found that the absorption edges of the two impurity-doped powder samples slightly shifted toward the high photon energy side (i.e., blue-shift behavior) relative to that of the undoped powder sample. The width of the optical bandgap (Eg) was estimated from Tauc plots based on the relationship $(\alpha$ hv)² \propto (hv – Eg), where hv is the photon energy. The optical bandgap energies were determined to be 2.48, 2.49, and 2.50 eV for the BiVO₄, BiVO₄:W, and BiVO₄:Mo powder samples (Table 1) by extrapolation of the onset of the dropping part to the *x*-axis (photon energy, eV) in the Tauc plots (as shown in Figure 7b by the dotted lines). The determined data are close to the results reported by Lei et al. [21] and Sharifi et al. [23].

Oshikiri and colleagues reported that the conduction band (CB) bottom of pristine $BiVO_4$ crystals is dominated by V 3d orbitals, and the valence band (VB) top is contributed by hybridized O 2p states and Bi 6s orbitals, according to the calculated results of $BiVO_4$ electronic structures based on the density-functional theory [32]. The hybridization of the O 2p and Bi 6s orbitals extends the top of VB, increases the mobility of photo-excited holes, and favors the photocatalytic degradation rate of organic dyes and pollutants [8]. This nature plays an important role in photocatalytic activity applications and the improvement of the photodegradation efficiency of Bi-based oxide photocatalysts. The obtained monoclinic $BiVO_4$ -based nanoparticles had an optical bandgap width of approximately 2.48–2.5 eV, which led to a characteristic of visible light absorption, confirming their applicability in visible light-driven photocatalysis.

2.2. Photocatalytic Degradation Performance of BiVO₄-Based Photocatalysts

The proposed photocatalytic reaction principle and mechanism [1] of a BiVO₄ photocatalyst under visible light illumination are illustrated in Figure 8. Knowing the relative positions of the VB and CB potentials of the oxide semiconductor with respect to the potentials of \bullet OH/H₂O and O₂/ \bullet O₂⁻ is helpful to understanding the photocatalytic reaction procedures and mechanisms. The positions of the conduction band minimum (CBM) and valence band maximum (VBM) are +0.3 eV and +2.78 eV, respectively [33,34]. In addition, the potential for the generation of \bullet OH [\bullet OH/H₂O] radicals is +2.68 eV for a normal hydrogen electrode (NHE) and that for \bullet O₂⁻ [O₂/ \bullet O₂⁻] radicals is +0.13 eV for an NHE [35]. Under the excitation of visible light, the photogenerated electrons transition from the VB to the CB of the BiVO₄ semiconductor, and photogenerated holes remain in the VB due to electron deletion. Photogenerated electrons and holes then migrate to the surface of the BiVO₄ nano-sized semiconductor. Subsequently, photogenerated electrons reduce O₂ to \bullet O₂⁻ and photogenerated holes convert H₂O into \bullet OH. Both \bullet O₂⁻ and \bullet OH support the photodegradation of RhB.



Figure 8. Schematic illustration of proposed photocatalytic reaction mechanism of BiVO₄ photocatalyst under visible illumination.

The photocatalytic degradation reaction is mainly related to the absorption and desorption of molecules on the surface of the photocatalyst. It is generally accepted that adding surfactants into the synthesis process could reduce the surface tension of the solution and make the precursors of oxide nanopartcles highly dispersive, therefore greatly increasing the photocatalytic performance [36,37]. Sodium dodecylbenzene sulfonate (SDBS) is a neutral anionic surfactant and is widely used as a morphology-directing agent. Zeng et al. reported that while adding SDBS into the reaction solution of hydrothermal synthesis did not change the crystal structure of BiVO₄-based nanoparticles, it could reduce the average particle size, increase the specific surface area, and rise hydroxyl content on the as-synthesized oxide nanoparticles to improve the photocatalytic activity properties [36].

The photocatalytic degradation rate of diluted RhB solution as a function of visible light illumination time for the three BiVO₄-based nanoparticles is shown in Figure 9a. Notably, the degradation of RhB dye by visible light irradiation was negligible due to its relatively stable structure, and the dark adsorption ability of these BiVO₄-based photocatalysts was approximately 4% (after standing in the dark for 30 min). For each mixed suspension, after visible light illumination for 120 min the photocatalytic activity efficiencies of different photocatalysts were found to be as follows: BiVO₄:Mo (86.8%) > BiVO₄:W (74.4%) > BiVO₄ (61.8%). The RhB solution degradation efficiency of the undoped BiVO₄ nanoparticles in this study is higher than that of hydrothermally synthesized pure BiVO₄ microcrystals reported by Tian et al. (55.9%) [20] and comparable to the photocatalytic activity of mBiVO₄ hollow microspheres with the pH of the reaction solution controlled at 4 (70%) [3]. Based on the above evaluation and analysis, it is found that a small amount of Mo doping is a simple and effective approach to significantly improve the photocatalytic activity.

When the initial concentration of organic dye is low, the pseudo-first-order approximation, expressed as Equation (1), can be utilized to quantitatively analyze the reaction rate of dye degradation [13,38].

1

$$n \left(C_0 / C_t \right) = kt \tag{1}$$

where C_0 and C_t represent the concentrations of dye in the mixed solution before and after light irradiation for t min, k is the degradation rate constant (min⁻¹), and t is the irradiation time (min). Each RhB aqueous solution photodegradation curve was analyzed by the pseudo-first-order degradation model as shown in Figure 9b, and the calculated

k values are listed in the last column of Table 1. The tendency of the degradation rate constant depends on the impurity dopant and corresponds well with the tendency of photodegradation efficiency. In addition, it is worth noting that the k value difference was more than double between the undoped and Mo-doped mBiVO₄ powder samples.



Figure 9. (a) Photocatalytic activity and (b) the first-order kinetics for degradation of diluted RhB solution by BiVO₄-based nanoparticles under visible light irradiation.

Figure 10 presents recycled results of BiVO₄:Mo nanoparticles under visible light irradiation. After three photodegradation reaction cycles, the removal efficiency of RhB dye was still at 80% compared to the performance of the fresh oxide nanoparticle photo-catalyst (~87%), indicating stability. The monoclinic BiVO₄ nanoparticles doped with W and Mo enhanced the photocatalytic activity because the dopants enhanced the density of photogenerated carriers, reduced charge-transfer resistance, and minimized the recombination ratio of photoexcited electron–hole pairs [11,13]. Moreover, the surface condition and surface area play critical roles in photocatalytic activity. It can be well summarized that the photocatalytic activity is not only related to the specific surface area associated with the morphology and diameter of the nano-sized BiVO₄-based photocatalysts; it also determines the charge generation and separation efficiency of the electron–hole pairs and efficient suppression of electron–hole recombination ability, which are correlated with their compositions and crystallinity.



Figure 10. Stability of BiVO₄:Mo nanoparticles in photocatalytic degradation of diluted RhB solution.

3. Materials and Methods

3.1. Chemicals and Synthesis Procedures of BiVO₄-Based Nanoparticles

Three kinds of bismuth vanadate (BiVO₄)-based powder samples, including undoped, W-doped, and Mo-doped BiVO₄, were synthesized using a hydrothermal method. First, stoichiometric amounts of bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O, Alfa Aesar, Ward Hill, MA, USA) and ammonium metavanadate (NH₄VO₃, Acros, Geel, Belgium) were individually dissolved in 2M nitric acid (HNO₃, J.T. Baker, Phillipsburg, NJ, USA) solution (10 mL), and each mixture was stirred for 30 min at room temperature (RT). Following this, 2.5 mg sodium dodecylbenzene sulfonate (SDBS, Sigma-Aldrich, Burlington, MA, USA) was added to the former as the morphology-directing agent [39]. The stoichiometric amount of W or Mo sodium salt was added to the latter to prepare the impurity-doped BiVO_{4-x} precursors. Sodium tungstate dihydrate (Na₂WO₄·2H₂O, Alfa Aesar), and sodium molybdenum oxide dihydrate (Na2MoO4.2H2O, Alfa Aesar) were selected as the raw materials for the W and Mo ion sources, respectively. The impurity doping levels were fixed at 2 at% $(M/(V + M), M = W \text{ or } M_0)$ in each resultant solution for the preparation of the impurity-doped samples. Following this, the 2 mixtures (Bi and V ions precursors) were mixed together in molar ratio of 1:1 and again stirred for 30 min at RT to obtain a stable and homogenous yellow precursor solution. Each chemical used in this study was an analytical grade reagent. The pH value of the reaction solutions was adjusted to 4 by adding an appropriate amount of NaOH solution. The as-prepared precursor solution was transferred into a 45 mL capacity Teflon-lined stainless-steel autoclave (Parr Instrument Company, model 4744, Moline, IL, USA), and the hydrothermal reaction synthesis was performed at 200 °C for 8 h under autogenous pressure. After the autoclave naturally cooled to RT, the Bi-based oxide precipitates were collected and washed 3 times with distilled water and once with ethanol before finally being dried at 60 °C for 10 h in the atmosphere.

3.2. Physical Properties Characterization and Photocatalytic Activity Measurement

The crystal structure of the as-prepared products was examined on an X-ray diffractometer (Bruker, Billerica, MA, USA) in the region of $2\theta = 10^{\circ} - 70^{\circ}$ using Cu K α radiation. The morphologies and particle sizes of the as-synthesized BiVO₄-based powders were observed and investigated with a Hitachi S-4800 scanning electron microscope (SEM, Tokyo, Japan) and JEOL JEM2100F transmission electron microscope (TEM, Tokyo, Japan). The surface area of the oxide powders was measured using the BET technique using N₂ adsorption/desorption isotherms with a Micromeritics ASAP2020 surface area and porosimetry system (Norcross, GA, USA). The elemental compositions and core-level binding energies were examined and recorded with a ULVAC-PHI PHI 5000 VersaProbe X-ray photoelectron spectroscope (XPS, Kanagawa, Japan). The electron spin resonance (ESR) spectra were collected with a Bruker EMX-10 electron paramagnetic resonance (EPR) spectrometer (Bremen, Germany) operating in the X-band frequency at approximately 9.83 GHz and 15 mW. The Raman spectra were examined and collected with a Nanobase XperRAM S Raman spectrometer (Seoul, South Korea) with an excitation wavelength of 532 nm. Fluorescence (FL) emission spectra were measured using a Shimadzu RF-5301PC spectrofluorophotometer (Koyoto, Japan) with a Xenon lamp as a 350 nm excitation light source. The near UV-visible absorption spectra were recorded on a JASCO V-770 UV-Vis/NIR spectrophotometer (Oklahoma City, OK, USA), which was used for a reflectance standard UV-Vis diffuse reflectance experiment in the wavelength range of 300-800 nm.

The photocatalytic activity of the BiVO₄-based nanoparticles was evaluated by measuring and analyzing the photodegradation efficiency of dilute Rhodamine B (RhB) solution under visible light at different times. The Bi-based oxide photocatalyst (0.01 g) was added into the as-prepared aqueous solution (100 mL) containing RhB dye (10 mg/L). In the dark condition, the mixture was stirred for 30 min to achieve the adsorption saturation of each species of photocatalyst suspension. Subsequently, the mixture was subjected to 300 W visible light illumination using an Xe lamp (500 W, $\lambda \ge 400$ nm). At specified time intervals, the suspension (0.8 mL) was collected by centrifugation at 500 rpm for 5 min

for the next measurement. The concentration of RhB was determined by measuring the absorption characteristics on a Hitachi U-2900 double-beam spectrophotometer (Tokyo, Japan). Cycling experiments were carried out to evaluate recyclability and stability of photocatalytic performance for developing the BiVO₄-based photocatalyst.

4. Conclusions

Undoped, W-doped, and Mo-doped BiVO₄ nanocrystalline particles were successfully prepared by the green hydrothermal route. These hydrothermally synthesized products had a single-phase monoclinic structure and high crystallinity. Results showed that lightly doping mBiVO₄ with W or Mo could modify the surface morphology, alter the particle shape, refine the particle size, and thereby increase the specific surface area. In addition, W or Mo ions partly replaced V⁵⁺ in mBiVO₄ crystals, both increasing the density of oxygen vacancies and promoting their n-type character. Such features helped to enhance the photocatalytic activity. The W- and Mo-doped BiVO₄ nanoparticles showed higher photocatalytic activity for photodegradation of diluted RhB solution than the undoped BiVO₄ nanoparticles, and the BiVO₄:Mo photocatalyst exhibited the best photodegradation efficiency of almost 87% under visible light illumination for 120 min. The enhanced photocatalytic degradation efficiency was related to neither the specific surface area value nor the generation/recombination rate of the photogenerated charge carriers of the asprepared oxide semiconductor photocatalysts.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/catal13030475/s1, Figure S1: SEM micrographs of hydrothermally synthesized BiVO₄-based nanoparticles. (a) undoped, (b) W-doped, and (c) Mo-doped BiVO₄ samples, Figure S2: (a) W 4f and (b) Mo 3d core-level spectra of hydrothermally synthesized BiVO₄:W and BiVO₄:Mo powder samples, respectively.

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