

Research Article

Preparation of a Leaf-Like BiVO₄-Reduced Graphene Oxide Composite and Its Photocatalytic Activity

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We prepared a unique leaf-like BiVO₄-reduced graphene oxide (BiVO₄-rGO) composite with prominent adsorption performance and photocatalytic ability by a single-step method. Multiple characterization results showed that the leaf-like BiVO₄ with average diameter of about 5 μm was well dispersed on the reduced graphene oxide sheet, which enhanced the transportation of photogenerated electrons into BiVO₄, thereby leading to efficient separation of photogenerated carriers in the coupled graphene-nanocomposite system. The characterization and experiment results also indicated that the outstanding adsorption ability of such composite was closely associated with the rough surface of the leaf-like BiVO₄ and doped rGO. The surface photocurrent spectroscopy and transient photocurrent density measurement results demonstrated that the doped rGO enhanced separation efficiency and transfer rate of photogenerated charges. As a result, the BiVO₄-rGO exhibited higher photocatalytic capacity toward the degradation of rhodamine B dye under visible-light irradiation compared with pure BiVO₄ and P25.

1. Introduction

In the world where energy shortage and environment pollution have become worse, semiconductor-based photocatalysis has attracted great attention over the past decades because of its potential applications in solar energy conversion and environmental purification [1–3]. To prepare high-activity photocatalysts, researchers have made numerous attempts to prepare new ones such as TiO₂, (BiO)₂CO₃, ZnO, and BiVO₄ [4–7]. Considering that visible light accounts for the largest proportion of the solar spectrum and artificial light, preparation of a high-activity visible-light-driven photocatalyst has become a hot topic at present [8].

As a visible-light-driven photocatalyst, BiVO₄ enjoys advantageous properties such as nontoxicity, low cost, and high stability against photocorrosion. The bandgap of monoclinic BiVO₄ is 2.4 eV, which means it can be successfully activated by visible light. Recently, more and more attention

has been paid to the synthesis of BiVO₄ of different sizes and shapes. Since the morphology of BiVO₄ will significantly impact its photocatalytic performance, researchers have synthesized BiVO₄ in various morphological shapes such as BiVO₄ nanosheets [9, 10], peanut-like BiVO₄ [11], spherical BiVO₄ [12], flower-like BiVO₄ [13], three-dimensional acicular sheaf BiVO₄ [14], and tube-like BiVO₄ [8], so as to better tune the photocatalytic capacities of materials and thus realize enhanced degradation of pollutants. However, pure BiVO₄ has limited efficiency in migration of photogenerated electron-hole pairs, which restricts its application in practical situations [15]. To solve this problem, great efforts have been conducted, for instance, incorporating reduced graphene oxide into the monoclinic BiVO₄ [16, 17].

It is a reliable way to improve the photocatalytic activity of pure BiVO₄ by coupling with graphene-related materials (e.g., reduced graphene oxide (rGO)). With two-dimensional conjugated structure and unique intrinsic

properties, graphene (as well as rGO) can serve as a supporting platform on which semiconductors can be dispersed and stabilized for being applied in catalysis [18]. rGO enjoys high electrical conductivity, high carrier mobility ($200000\text{ cm}^2/\text{V}$), high specific surface area ($2630\text{ m}^2/\text{g}$), and a bandgap which is almost zero [19–21]. Therefore, it is a preferred material for loading catalysts, transporting electrons, and stabilizing extraneous electrons. It is worth noting that graphene has outstanding electronic conductivity because of its high abundance of delocalized electrons in its π -conjugated electronic structure. In the graphene-composite coupled system, the high conductivity of graphene facilitates an effective transfer of photogenerated charges in the attached semiconductors, thus leading to efficient separation of photo-generated charge carriers [12, 22, 23].

There have been few comparative researches on lamellar BiVO_4 -graphene nanocomposite and microspherical silver-rGO- BiVO_4 composite [12, 22]. These researches revealed that the morphology of the catalyst has great influence on its photocatalytic activity. In this study, a single-step method was adopted to synthesize a leaf-like BiVO_4 -rGO composite, of which the photocatalytic activity was tested via degradation of rhodamine B.

2. Experiments

2.1. Materials. In this experiment, we used analytically pure chemicals including bismuth(III) nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Chengdu Kelong Chemical Company), ammonium metavanadate (NH_4VO_3 , Chongqing Chuandong Chemical Company), sodium hydroxide (NaOH , Chongqing Chuandong Chemical Company), nitric acid (HNO_3 , Chengdu Kelong Chemical Company), rhodamine B (RhB) dye (Tianjin Guangfu Fine Chemical Research Institute), and graphene oxide water solution (GO solution, $\geq 99.85\%$, with concentration of 2 mg/mL , Hengqiu Tech Company).

2.2. Synthesis of BiVO_4 -rGO Composite. Dissolve 0.01 mol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 50 mL of 2 mol/L HNO_3 solution, and then mark the solution as solution A. In contrast, dissolve 0.01 mol NH_4VO_3 in 50 mL of 2 mol/L NaOH solution, and then mark the solution as solution B. After that, add solution B dropwise to solution A while stirring for 30 min . Adjust the pH of the mixed solution to 7 by adding 2 mol/L NaOH solution dropwise. In addition, add 8.2 mL of 2.0 mg/mL GO solution to 20 mL of DI water, and then conduct sonication treatment in an ultrasonic bath for about 1 h . Subsequently, add GO solution to the BiVO_4 mixed solution followed by sonication treatment for another 1 h . After the above procedures, a homogeneous suspension is formed, and thus the sample can be obtained. Place the sample in a 100 mL Teflon-sealed autoclave at 200°C for 6 h before realizing the crystallization of BiVO_4 and GO composite and the reduction of GO. Conduct centrifugation treatment for the precipitate, wash it with deionized water several times, and then dry it in the vacuum freeze drier at -60°C for 24 h , finally obtaining the synthesized composite known as BiVO_4 -rGO (wherein

the mass percentage of rGO is 0.5%). For comparison, implement the same procedures to synthesize pure BiVO_4 .

2.3. Characterization. Scanning electron microscopy (SEM) images were obtained using a JSM-7800F JEOL emission scanning electron microscope; energy dispersive X-ray (EDX) images were obtained using an EDX-100A-4; powder X-ray diffraction (XRD) spectra were obtained using a Rigaku D/Max-rB diffractometer with $\text{Cu K}\alpha$ radiation. The scanning angle 2θ ranged between 10° and 70° . UV-visible diffuse-reflectance spectroscopy (UV-Vis DRS) was performed using Hitachi U-3010 UV-Vis spectrometer. Fourier transform infrared spectroscopy (FTIR, IRPrestige-21, Shimadzu, Japan) analysis of the composite was conducted using FTIR spectrophotometer by using KBr as a reference sample. An Al K α X-ray source (Thermo Fischer Scientific, K-Alpha, UA) was adopted to conduct X-ray photoelectron spectroscopy (XPS) characterization. Photoelectrochemical properties were evaluated using a CHI Electrochemical Workstation (CHI 760E, Shanghai Chenhua, China). The sample for electron spin resonance (ESR) measurement was prepared by mixing photocatalyst powder samples in a 50 mM DMPO solution tank (aqueous dispersion for $\text{DMPO}\cdot\text{OH}$ and methanol dispersion for $\text{DMPO}\cdot\text{O}_2^{\cdot-}$). The Brunauer-Emmett-Teller (BET) surface area measurements and evaluation of the porosities of the samples were conducted on the basis of nitrogen adsorption isotherms measured at 400°C using a gas adsorption apparatus (Gemini VII 2390, Micromeritics Instrument Corp., Norcross, GA, USA).

2.4. Evaluation of Photocatalytic Activity. The photocatalytic activities of the samples were evaluated via photodegradation of RhB using a 500 W Xe lamp as visible-light irradiation source at room temperature. In this experiment, first add 0.10 g catalyst to 100 mL of a 5 mg/L RhB aqueous solution, and then keep magnetically stirring for 30 min in the dark to obtain good dispersion and reach adsorption-desorption equilibrium between the dye and the catalyst. After that, place the solution in a 250 mL beaker, which is located 350 mm away from the 500 W Xe lamp. Collect the solution once for every 2 h of irradiation, and then subject it to centrifugation at 10000 r/min for removing catalysts, and finally test the absorbance of RhB in the solution. The concentration of the remaining dye was spectrophotometrically monitored according to the absorbance of the solutions at 552 nm . For comparison, the control experiments were performed with pure BiVO_4 , P25, and BiVO_4 -rGO (with different mass percentages of rGO), or without any catalyst under the same condition. To investigate the effect of rGO dosage on the photocatalytic property of the photocatalyst, the BiVO_4 -rGOs with rGO wt% of 0.25 , 0.5 , and 1 were synthesized, respectively.

3. Results and Discussion

3.1. SEM-Based Morphology Analysis. Scanning electron microscopy (SEM) was used to study the sizes and morphologies of the prepared samples. As shown in

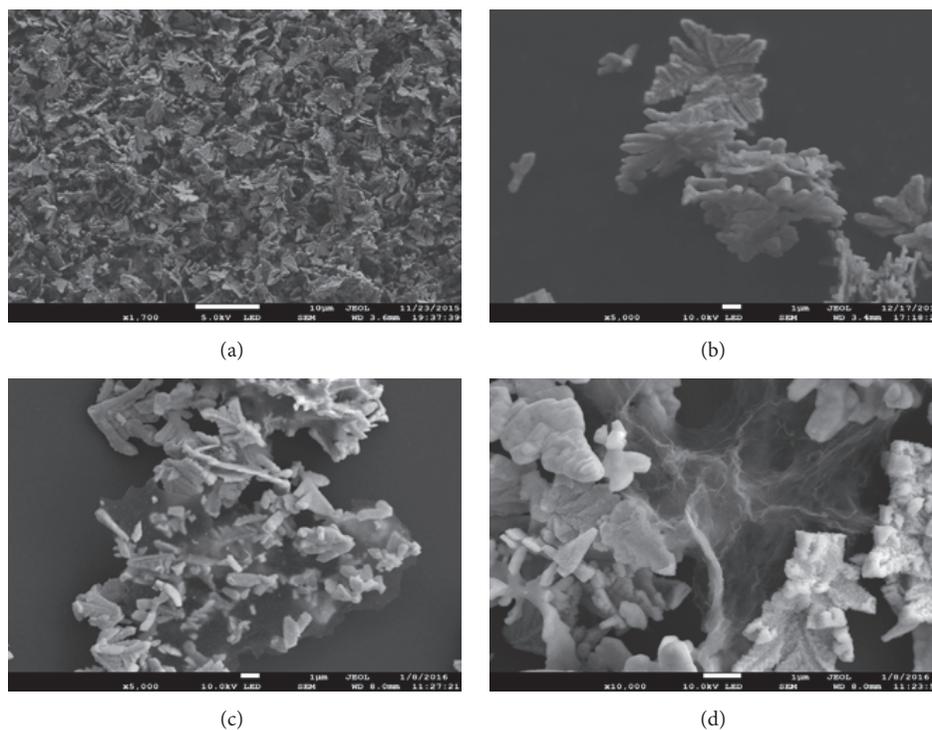


FIGURE 1: SEM images of ((a), (b)) pure BiVO_4 and ((c), (d)) BiVO_4 -rGO.

Figure 1, each sample has a unique leaf-like structure consisting of BiVO_4 crystal grains of which the average diameter is about 5 μm , and the rGO sheet within is easy to be observed. According to Figures 1(c) and 1(d), it can be seen that the two leaf-like BiVO_4 structures are loaded on the rGO sheets. Since BiVO_4 and rGO sheets are closely in contact with each other, transportation of electrons photogenerated in BiVO_4 can be enhanced, thereby leading to efficient separation of photogenerated carriers in the coupled rGO-composite system. In conclusion, this material is expected to have enhanced photocatalytic activity.

3.2. EDX-Based Composition Analysis. The chemical composition of BiVO_4 -rGO was measured by studying its EDX spectrum. Figure 2 shows that BiVO_4 -rGO is mainly composed of elements Bi, C, O, and V. Based on the elemental mapping images, we can draw the following conclusion. First, the leaf-like particles are bismuth vanadate, because their distributions of Bi, O, and V are almost the same; second, the surface of BiVO_4 is covered with a layer of rGO film, because the color of C element is determined by rGO film's position. According to the SEM and EDX results, it can be known that the leaf-like BiVO_4 particles are successfully loaded on the surface of the rGO film, which is consistent with XRD results.

3.3. XRD Pattern Analysis. The phase structures of the composites were characterized by X-ray diffraction (XRD) measurement and the XRD patterns are shown in Figure 3.

The sharp XRD peaks indicate that the BiVO_4 is in high crystallinity. From this figure, we can see that almost all the diffraction peaks (110, 010, 121, 040, 200, 211, 150, 240, 161, etc.) of the pure BiVO_4 and BiVO_4 -rGO could be ascribed to the monoclinic BiVO_4 (JCPDS 14-0688) [24] which is the most active phase of three phases of BiVO_4 under visible-light irradiation [25]. This explains why the photocatalysts remain in a monoclinic structure and why the phase of BiVO_4 remains unchanged after the addition of GO. An insignificant peak (002, with blue color) of rGO at around 25° can be observed while no characteristic peak of GO at around 12° can be found, which indicates that GO has been well reduced to rGO through the photocatalytic reduction process [18, 26]. The XRD analysis also shows that the phase of BiVO_4 remains unchanged after the addition of GO.

3.4. Analysis of Optical Properties Based on UV-Vis DRS. The optical absorption property of the semiconductor has been regarded as a key influencing factor on its photocatalytic performance. Figure 4 shows representative spectra of pure BiVO_4 and BiVO_4 -rGO, respectively, from which we can see that the absorption spectrum of BiVO_4 -rGO is nearly the same as that of pure BiVO_4 , and the spectrum of BiVO_4 -rGO is above that of pure BiVO_4 . These results verify that the incorporation of rGO can lead to significantly increased absorption of visible light, therefore increasing the utilization of visible light.

Moreover, the energy band structure of semiconductor is also an important factor determining its photocatalytic

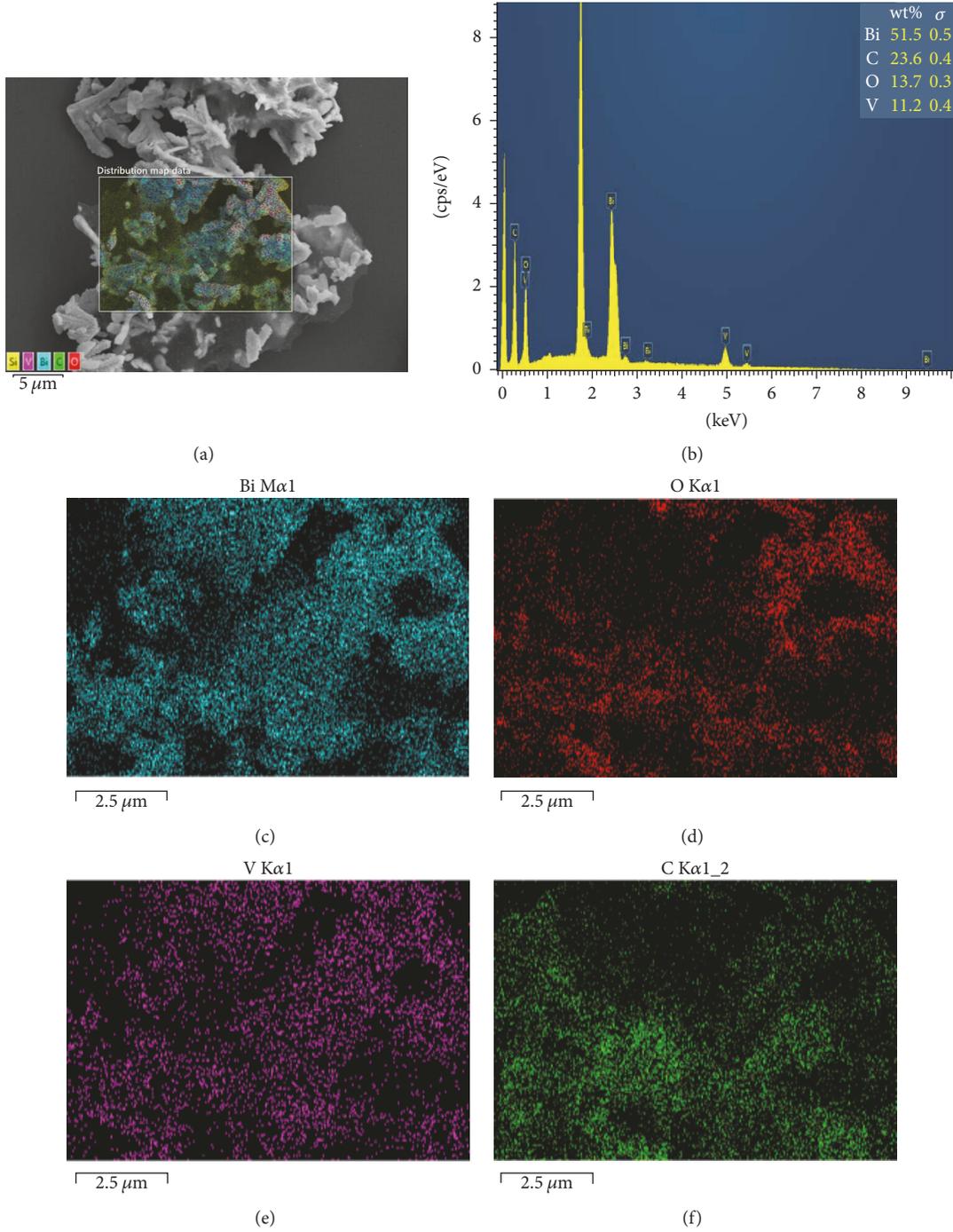


FIGURE 2: (a) SEM image of composite BiVO₄-rGO; (b) EDX spectrum of composite BiVO₄-rGO; ((c)–(f)) SEM elemental distribution mappings of Bi, O, V, and C.

activity. The relationship of absorbance and incident photon energy $h\nu$ can be described by

$$A h\nu = C (h\nu - E_g)^{1/2}. \quad (1)$$

In this equation, A represents the absorption coefficient, E_g represents the bandgap energy, h represents Planck's constant, ν represents the incident light frequency, and

C denotes a constant. The bandgap energy (E_g) of the photocatalyst can be estimated by a plot depicting $(A h\nu)^2$ versus $h\nu$ [27, 28]. The estimated bandgap energies of pure BiVO₄ and BiVO₄-rGO were measured to be 2.375 eV and 2.29 eV, respectively. The absorption edges of BiVO₄-rGO and pure BiVO₄ were measured to be 541.48 nm and 522.1 nm, respectively.

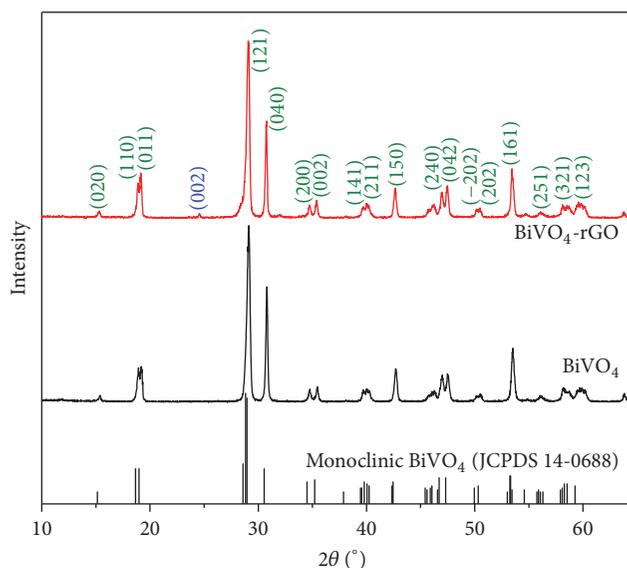


FIGURE 3: XRD patterns of pure BiVO_4 , BiVO_4 -rGO, and monoclinic BiVO_4 (JCPDS 14-0688).

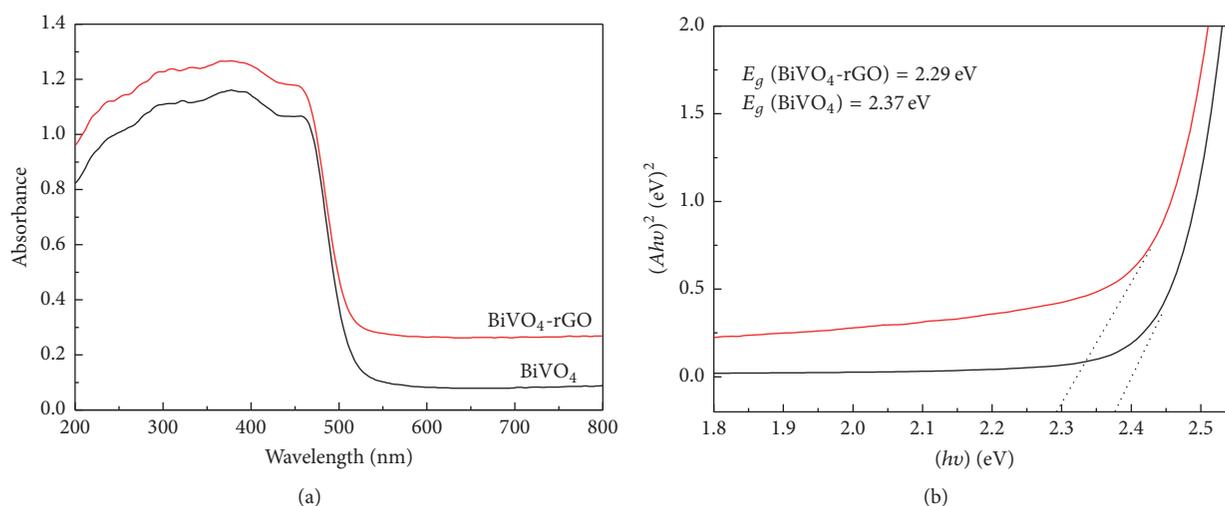


FIGURE 4: (a) UV-Vis DRS spectra. (b) The relationship between $(Ah\nu)^2$ and the photon energy $(h\nu)$ of the as-synthesized pure BiVO_4 and BiVO_4 -rGO.

3.5. FTIR-Based Chemical States Analysis. In order to ensure an efficient transfer of rGO and to characterize the carbon species, FTIR was used to obtain further insights into the reduction of GO. Figure 5 shows the FTIR spectra of GO, GR, BiVO_4 , and BiVO_4 -rGO, respectively. We can observe a strong absorption band of GO at 3410 cm^{-1} due to the O-H stretching vibration. The characteristic peaks at 1736 , 1628 , 1406 , and 1089 cm^{-1} can be ascribed to carboxyl or carbonyl C=O stretching, carboxyl-OH stretching, C=C stretching, phenolic C-OH stretching, and alkoxy C-O stretching, respectively [29, 30]. In contrast to GO, the various oxygen-containing groups ($800\text{--}1900\text{ cm}^{-1}$) in BiVO_4 -rGO and GR are significantly decreased or even disappeared, indicating that the hydrothermal synthesis is an effective method for reducing GO into rGO. In the case of the BiVO_4 -rGO, the

typical absorption peaks of GO are dramatically weakened or even disappeared as compared with those of the pure GO, which verifies the reduction action of GO. The broad absorption cases at low frequency (below 1000 cm^{-1}) are associated with ν_1 (VO_4) and ν_3 (VO_4) [31]. All the results show that, in our study work, we can successfully prepare a composite catalyst which incorporates rGO as a platform.

3.6. XPS-Based Chemical States Analysis. XPS was used to evaluate the chemical and bonding environments of loaded BiVO_4 -rGO, and results are shown in Figure 6. As shown in Figure 6(a), the scanned spectrum of BiVO_4 -rGO is within the range between 0 and 800 eV, from which we can find that this composite consists of elements Bi, O, V, and C. Figure 6(b) shows the binding energies for Bi $4f_{7/2}$ and Bi

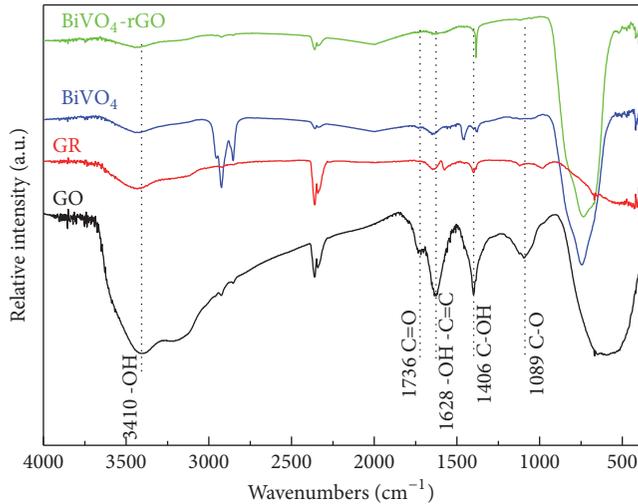


FIGURE 5: FTIR spectra of GO, GR, pure BiVO_4 , and BiVO_4 -rGO.

$4f_{5/2}$ to be 158.8 and 164.1 eV, respectively, which is closely associated with the Bi^{3+} peak in the monoclinic BiVO_4 [32]. Figure 6(c) shows the Cls XPS spectrum, in which we can see two characteristic peaks that are caused by the oxygenated ring C bonds (284.6 eV for C-C, C=C, and C-H and 287.0 eV for the C-O bond) [33]. These results indicate that some oxygen-containing functional groups are loaded on the rGO surface. Due to the presence of these groups, pollutants can be absorbed by catalysts more easily, and the photocatalytic effect of the catalyst can be enhanced. However, in the Cls XPS spectra of BiVO_4 -rGO, the relative intensities of the three components associated with C-O/C-O bonds decrease significantly, which indicates that some of the oxygen functional groups were reduced during the reduction process [34]. Although the GO makes no contribution to the transfer of electron because of nonconductivity, the GO after reduction (rGO) is significantly helpful. According to Figure 6(e), it can be seen that the peaks at binding energies of 524.1 ($\text{V}2p_{1/2}$) and 516.3 eV ($\text{V}2p_{3/2}$) belong to the split signal of $\text{V}2p$, and the $\text{V}2p$ peak is ascribed to V^{5+} [31].

3.7. Charge Separation Based on SPS and TPD. The photocatalytic ability of composite is also largely dependent on its capability of separating and transferring charges [35, 36]. The steady-state surface photocurrent spectroscopy is an effective approach to reveal the charge transfer efficiency of a semiconductor. In order to investigate the impact of rGO on the charge separation of BiVO_4 , SPS was conducted in air atmosphere, and the SPS results are shown in Figure 7(a), from which we can observe strong signals for both samples. The deposited rGO on BiVO_4 could enhance the SPS response. Moreover, a stronger SPS response can lead to a higher charge separation rate [37]; therefore, it can be concluded that rGO can lead to enhanced charge separation of BiVO_4 .

Photoelectrochemical measurements were conducted to study the excitation, separation, transfer, and recombination

TABLE 1: The degradation efficiency after 8 h and adsorption efficiency after 30 min of different photocatalysts.

Sample	Adsorption efficiency	Degradation efficiency
P25	0.04%	13%
BiVO_4	14%	37%
BiVO_4 -rGO 0.25%	17%	49%
BiVO_4 -rGO 1%	21%	59%
BiVO_4 -rGO 0.5%	29%	75%

of photogenerated charge carriers [38]. As shown in Figure 7(b), BiVO_4 -rGO electrode displays a prompt, steady, and reproducible photocurrent response during repeatedly switching on/off Vis irradiation, and lower photocurrent density is observed in the case of BiVO_4 . The enhanced photocurrent of the BiVO_4 -rGO electrode is associated with high photogenerated charge separation efficiency and high charge transfer rate in the composite. The rGO serves as an acceptor and also a transporter for the electrons excited by visible-light energy and generated from BiVO_4 , so as to inhibit the recombination of photogenerated electron-hole pairs effectively.

3.8. Photocatalytic Activity for Degradation of RhB. Figure 8 shows the photodegradation rates of RhB under visible-light irradiation by using BiVO_4 -rGO (with rGO wt% of 0.25%, 0.5%, and 1%), pure BiVO_4 , and P25, respectively. For comparison, the results of degradation of RhB without involvement of catalysts are also shown. Prior to irradiation, the mixture of the dye and catalyst was stirred in the dark for 30 min to attain adsorption-desorption equilibrium. Moreover, the photostability test was also evaluated.

From Figure 8(a) and Table 1, we can see that the concentrations of RhB in the presence of photocatalysts gradually decrease with the extending of visible-light irradiation time, while the concentration of RhB without the involvement of catalysts decreases insignificantly. This result indicates that the degradation of the RhB solution is affected by photocatalytic reaction under visible-light irradiation. After 8 h of irradiation, only about 3% of RhB was degraded without catalyst, which is mainly due to the self-sensitization induced photodegradation of RhB. In contrast, there were about 13%, 37%, 49%, 59%, and 75% of RhB photocatalytically degraded with P25, pure BiVO_4 , BiVO_4 -rGO-0.25%, BiVO_4 -rGO-1%, and BiVO_4 -rGO-0.5%, respectively. After stirring in the dark for 30 min, the adsorption percentages of P25, pure BiVO_4 , BiVO_4 -rGO-0.25%, BiVO_4 -rGO-1%, and BiVO_4 -rGO-0.5% were 0.04%, 14%, 17%, 21%, and 29%, respectively, which indicates that the leaf-like BiVO_4 photocatalyst is of excellent adsorption performance.

As shown in Figure 8(a), the photocatalytic ability of pure BiVO_4 is much stronger than that of P25 under visible-light irradiation. This is because the light response range of BiVO_4 is larger than that of P25 and the rough surface of special leaf-like BiVO_4 (in Figure 1, SEM pictures) can increase the reaction interface. In addition, the degradation rate of RhB when using the BiVO_4 -rGOs as a catalyst was

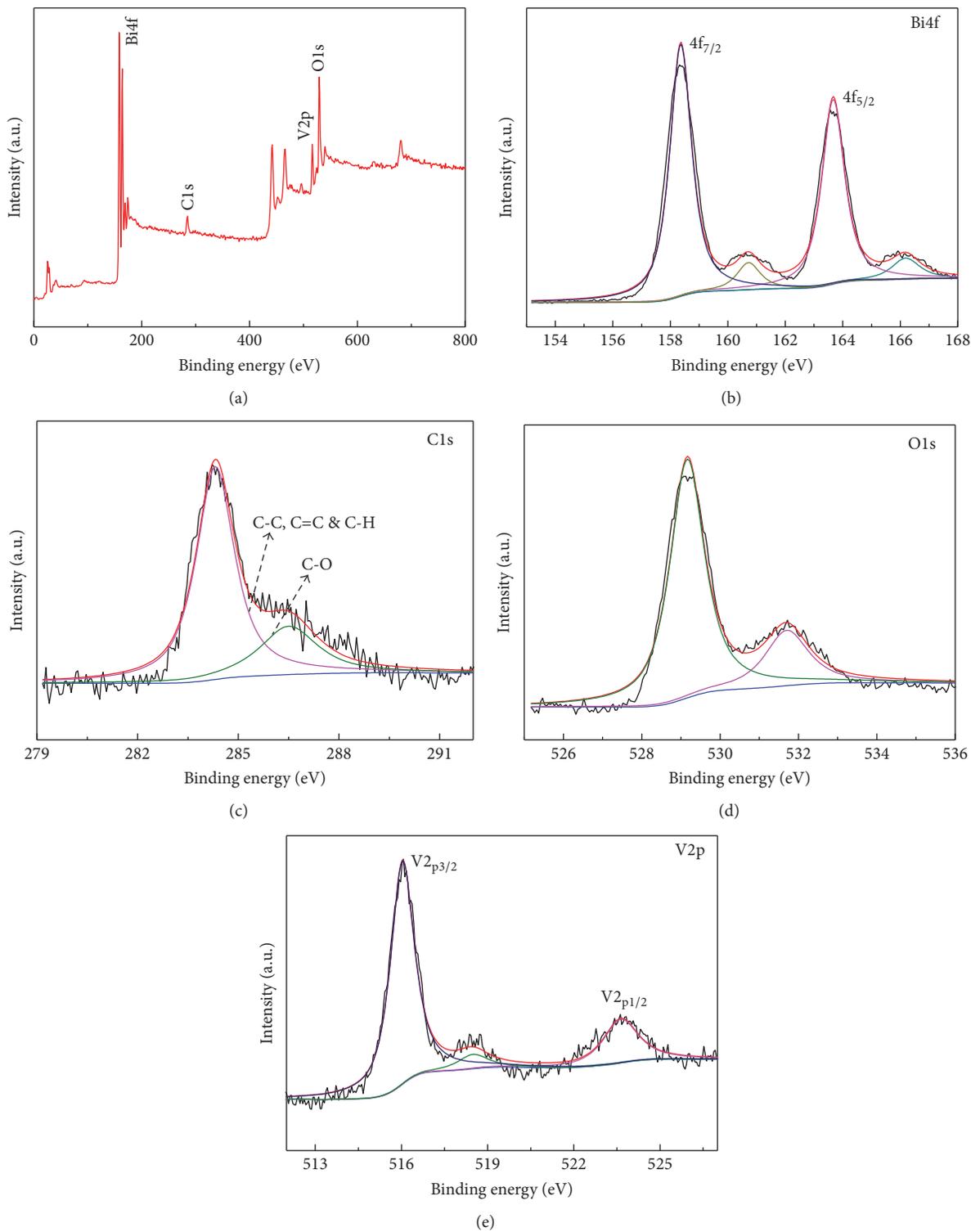


FIGURE 6: XPS spectra of the as-obtained BiVO₄-rGO. (a) Survey XPS spectrum; (b) Bi4f spectrum; (c) C1s spectrum; (d) O1s spectrum; (e) V2p spectrum.

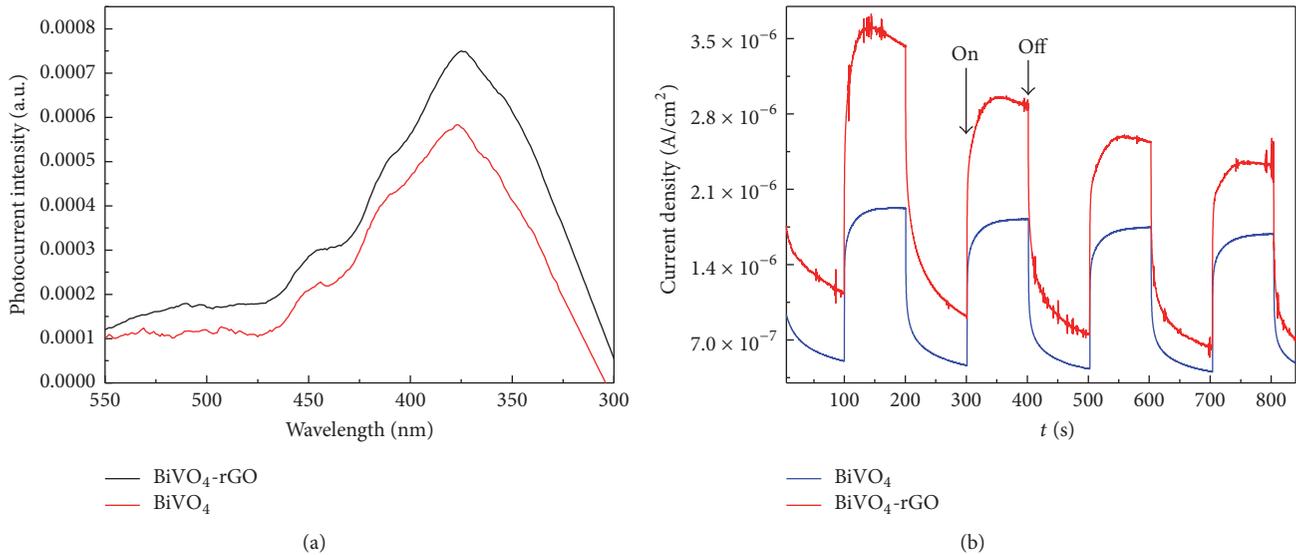


FIGURE 7: (a) The surface photocurrent spectroscopy (SPS) images of the as-obtained BiVO_4 -rGO and pure BiVO_4 . (b) The transient photocurrent densities (TPD) of the as-obtained BiVO_4 -rGO and pure BiVO_4 .

TABLE 2: Characteristics obtained from nitrogen desorption isotherms.

Sample	Mean pore size (nm)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Surface area ($\text{m}^2 \text{g}^{-1}$)
BiVO_4	0.558	0.006381	2.199
BiVO_4 -rGO 0.5%	3.5915	0.016921	8.0929

higher than that when using pure BiVO_4 as a catalyst. This is mainly due to the fact that BiVO_4 -rGO has larger BET surface area and pore volume (Table 2), which further enhances the contact area between BiVO_4 -rGO and organic contaminants. Moreover, the high electrical conductivity and high carrier mobility from rGO enhance the transfer of photogenerated electrons in the BiVO_4 , thereby leading to efficient separation of photogenerated carriers in the coupled BiVO_4 -rGO system and an increased photoconversion efficiency, which is consistent with the results of UV-Vis DRS, SPS, and TPD. We also studied the effect of the dosage of rGO on the photocatalytic properties of the photocatalyst, which can be ordered as BiVO_4 -rGO-0.5% > BiVO_4 -rGO-1% > BiVO_4 -rGO-0.25%, indicating that the dosage of rGO indeed has a significant effect on both adsorption and degradation. The optimal dosage of rGO was finally determined as 0.5%. Although rGO can increase the surface area and facilitate the transfer of photogenerated electrons in the BiVO_4 , an excessive dosage of rGO may lead to the shielding of the active sites of the photocatalysts, decreased contact area between BiVO_4 and light illumination, and lowered efficiency of light passing through the reaction solution, thereby reducing the photoactivity of BiVO_4 -rGO composite [39].

Stability is another index greatly affecting the application of the catalyst. The stability of BiVO_4 -rGO has been investigated, and the results are shown in Figure 8(c), from

which we can see that there is no significant deactivation during the 4-cycle photodegradation process, and the slight decrease of photocatalytic activity is probably due to the mass loss during the centrifugation and washing process.

In order to investigate the photocatalytic mechanism, spin-trapping ESR technique was conducted to detect photo-generated radicals in the photocatalytic process, and results are shown in Figure 9. DMPO (5,5-dimethyl-1-pyrroline-N-oxide) is usually used for trapping radicals because of its capability of generating stable radicals such as the DMPO-hydroxyl radical ($\cdot\text{OH}$) and DMPO-superoxide radical ($\text{O}_2^{\cdot-}$). The ESR technique was adopted to monitor the reactive species generated under the visible-light irradiation in the presence of BiVO_4 -rGO and BiVO_4 in aqueous dispersion for DMPO- $\cdot\text{OH}$ and in methanol dispersion for DMPO- $\text{O}_2^{\cdot-}$, and the results are shown in Figure 9. From the 4 pictures, we can clearly observe the signals of superoxide ($\text{O}_2^{\cdot-}$) and hydroxyl ($\cdot\text{OH}$) radicals. The intensities of $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ signals of BiVO_4 -rGO increase significantly after 9 min of irradiation, as shown in Figures 9(a) and 9(b). Therefore, $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ are the main oxidative species for the BiVO_4 -rGO system which can react with RhB. As shown in Figure 9(c), the signal intensity of superoxide ($\text{O}_2^{\cdot-}$) of BiVO_4 -rGO is stronger than that of BiVO_4 , which can also be observed in Figure 9(d).

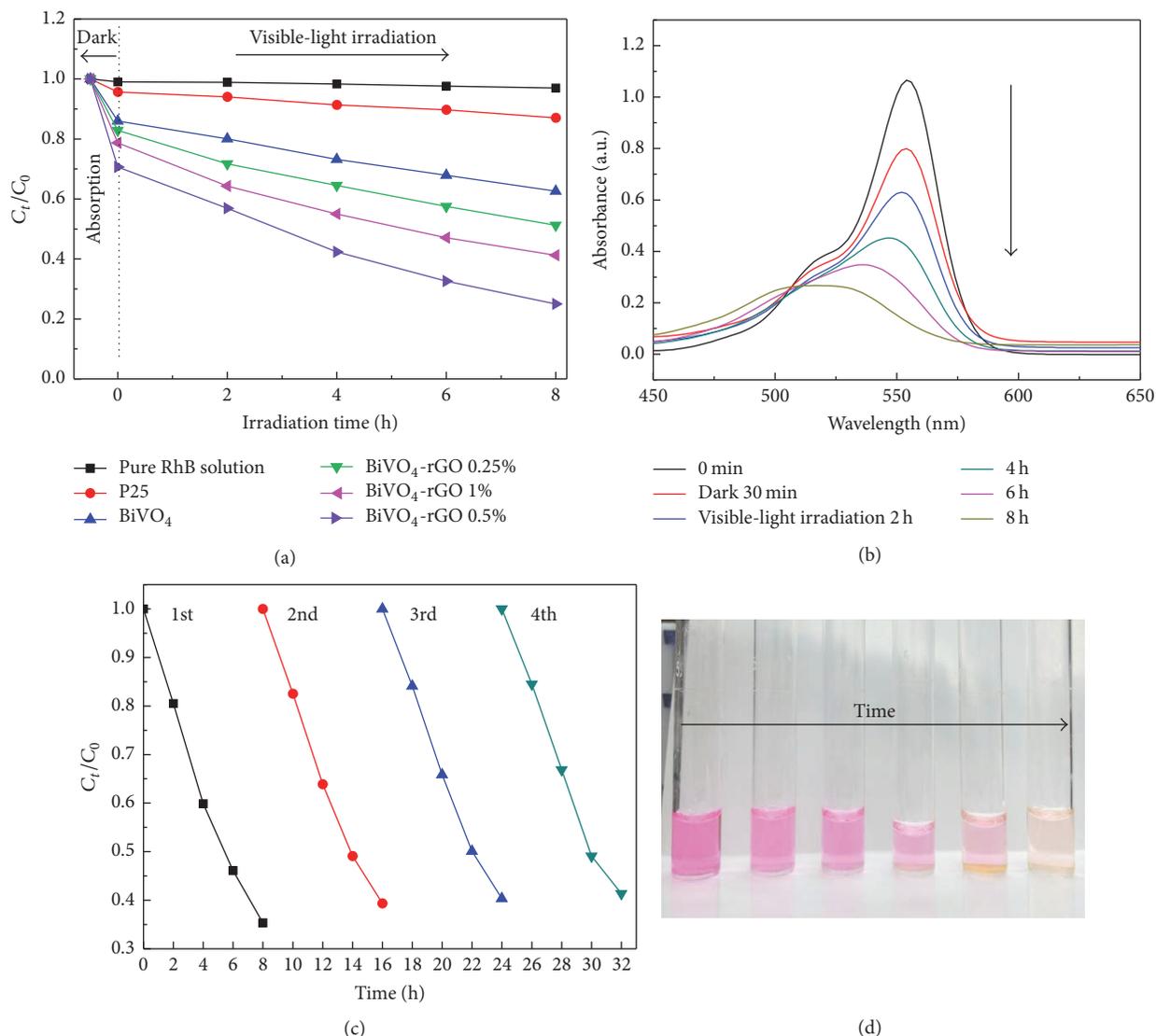


FIGURE 8: (a) The concentration ratio of the remaining RhB with different catalysts under visible-light irradiation. ((b), (d)) Photocatalytic performance of BiVO₄-rGO 0.5% for the decolorization of RhB as measured by UV-Vis DRS and pictures. (c) The photostability test of BiVO₄-rGO 0.5% for the cycling photodegradation of RhB under visible-light irradiation.

A possible reaction process is proposed in Figure 10. Electron-hole pairs are first generated on the BiVO₄ surface under visible-light excitation, and then photogenerated electrons are quickly transferred to rGO sheets via the percolation mechanism. After that, the electrons on rGO sheets react with O₂, resulting in $\cdot\text{O}_2^-$ radicals and $\cdot\text{OH}$. Finally, the dye molecules adsorbed on the active sites of BiVO₄-rGO are oxidized by the active species (h^+ , $\cdot\text{OH}$, and $\text{O}_2^{\cdot-}$). In the whole process, the rGO sheet serves as an electron mediator, which is of enhancing effect for the separation and transfer of electrons.

4. Conclusions

In summary, a simple and low-cost method was proposed for the controllable synthesis of leaf-like BiVO₄-rGO under gentle conditions. The as-synthesized composite BiVO₄-rGO

exhibited excellent performances in adsorption and photocatalytic degradation of RhB in aqueous solution. After being incorporated with rGO, the leaf-like BiVO₄ displayed an enhanced photocatalytic activity, enhanced light harvesting efficiency, and reduced charge recombination rate due to its unique morphological structure. In addition, the as-prepared BiVO₄-rGO showed good photocatalytic repeatability and stability under irradiation for a prolonged time. This research, in which a unique shaped semiconductor was combined with rGO, provides reference for designing novel hybrid photocatalysts that may effectively solve water-pollution issues.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

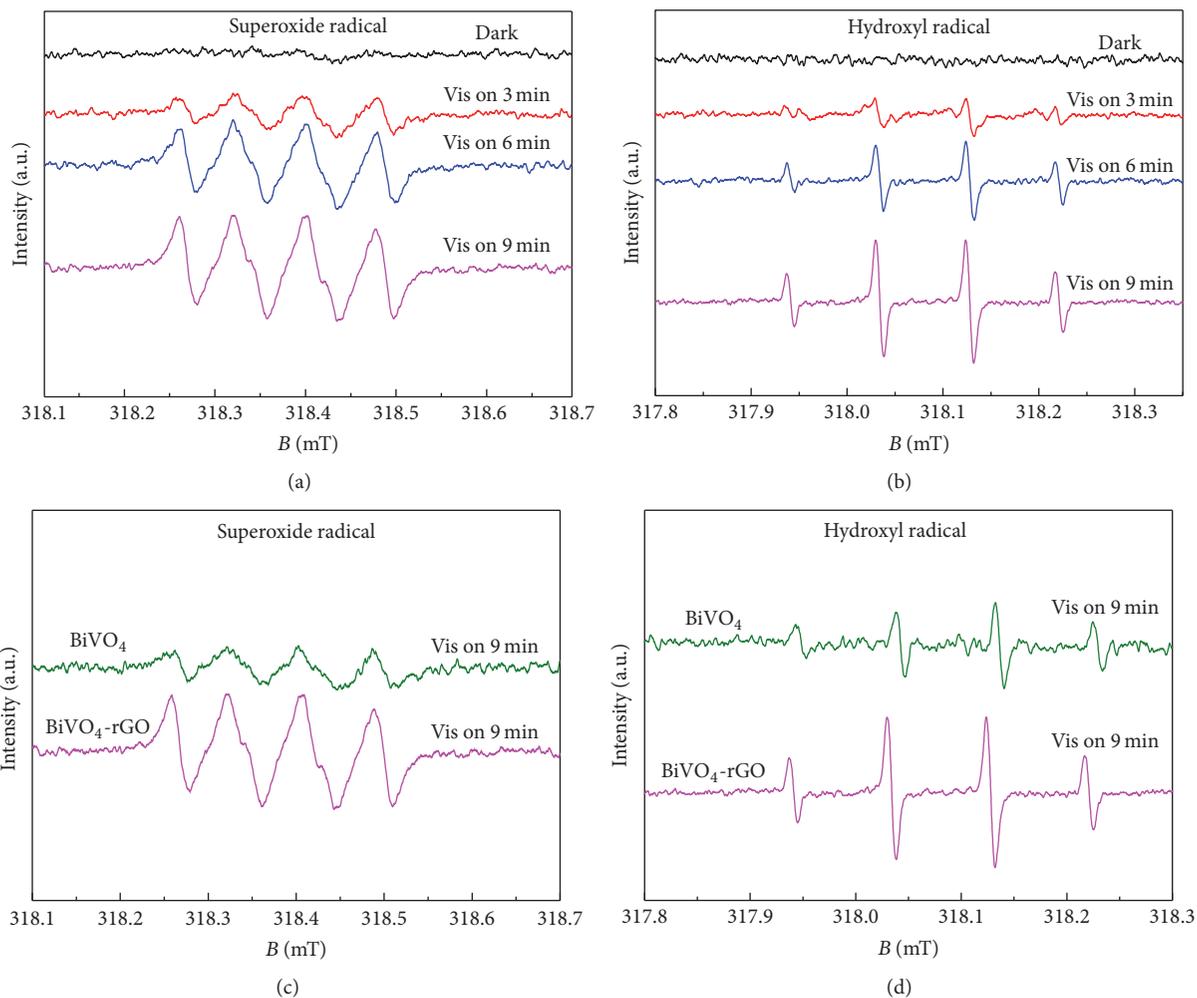


FIGURE 9: DMPO spin-trapping ESR spectra of BiVO_4 -rGO during different times (a) in aqueous dispersion for $\text{O}_2^{\cdot-}$ and (b) in methanol dispersion for $\cdot\text{OH}$; the DMPO spin-trapping ESR spectra of BiVO_4 -rGO and BiVO_4 under Vis irradiation for 9 min (c) for $\text{O}_2^{\cdot-}$ and (d) for $\cdot\text{OH}$.

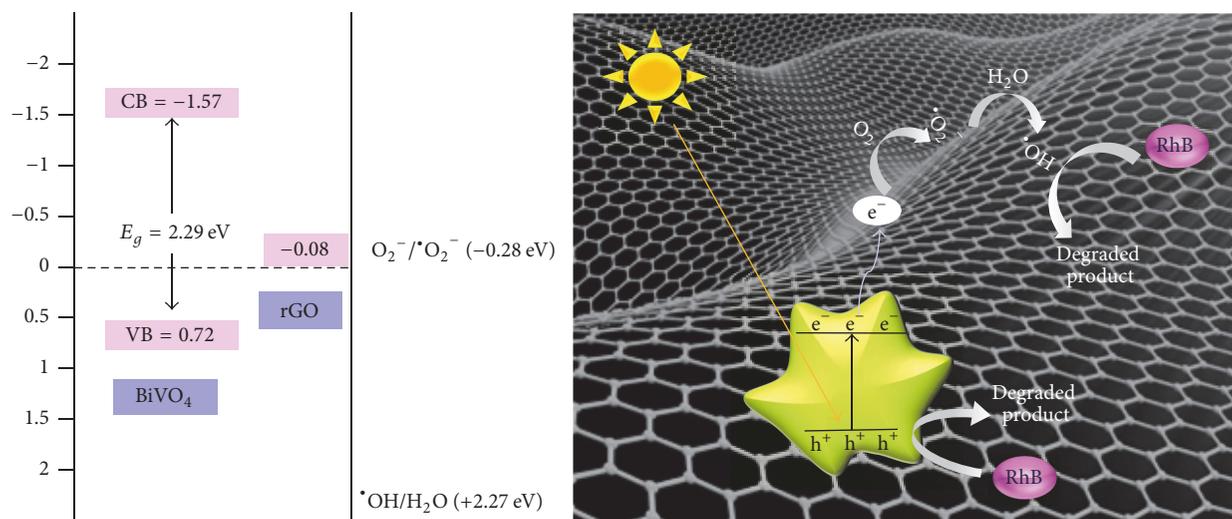


FIGURE 10: Photocatalytic reaction mechanism of BiVO_4 -rGO.

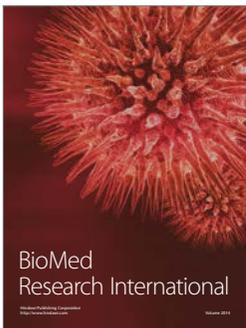
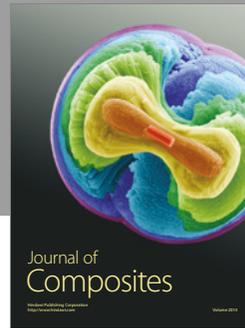
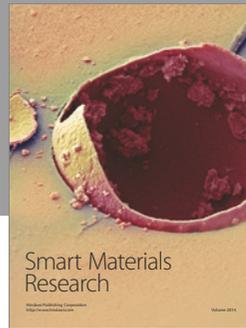
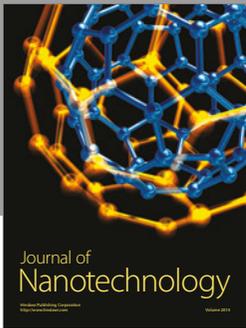
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