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Design, fabrication and characterization of photocatalyst Ni-doped BiVO₄ for high effectively degrading dye contaminant

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Abstract

Contaminated environment from textile industries have attracted global concern owing to the traits of organic pollutions with high stability against light and chemicals attacks. How to improve the preparation process of photocatalysts and reduce the cost is a considerable requirement for the wide application of photocatalytic wastewater treatment. The Ni-doped BiVO₄ (NBVO) process was improved to a facile and reliable hydrothermal method. Ni with a theoretical mass of 0.75% was added to BiVO₄ (BVO), which displayed outstanding photocatalytic activity and stability. Under visible light irradiation, the decolorization rate of 0.75% NBVO to Rhodamine B (RhB) can reach 96% within 75 min, and the removal efficiency can still achieve 86% after four successive cycles. The active ingredient •O₂− confirmed from capture experiments played an indispensable role and was hired to explain the possible photocatalytic mechanism. In addition, the enhanced photocatalytic activity of 0.75% NBVO should be ascribed to the increase in specific surface area (beneficial for adsorption) and the decline in impedance (favorable for photocarrier migration). 0.75% NBVO as a highly efficient visible-light-driven photocatalyst has a brighter prospect for wastewater treatment in the years ahead.

1. Introduction

Water pollution has posed a serious threat to environmental safety and human health [1]. Moreover, the amount of wastewater discharge is increasing with the development of global industrialization [2]. Textile dyes are organic pollutants produced during industrialization, such as methylene blue, methyl orange and RhB [3–6]. RhB can cause serious food safety, agricultural pollution and health problems because of the high stability against light, temperature, chemicals and microbial attacks [7]. Therefore, the removal of organic contaminant RhB has become increasingly important [8]. Various physical, chemical and biological methods have been employed to handle RhB. However, the poor effects so far have remained due to their respective limitations [9]. The use of solar energy photocatalyst for wastewater removal is a green, environmentally friendly, convenient and safe method to treat RhB [10].

Since Honda first discovered the water decomposition trait of TiO₂ photoelectrodes [11], it has been a hot topic that the application of metal oxide semiconductors in the field of photocatalysis and photoelectron chemistry [12–17]. Nevertheless, it is a pity that various defects, including wide band gap, fast recombination of photogenerated electron-hole pairs and low hydroxy radical (•OH) quantum yield (•OH has been frequently recognized as the major reactant responsible for the photocatalytic oxidation of organic compounds), have been discovered one after another [18, 19]. As a result, many researchers have developed a large number of other photocatalysts (typical Bi₂O₃, ZnO, CdS and MoS₂ [20–23]) to attempt to replace TiO₂. BVO materials have attracted tremendous attention due to their suitable energy band structure, low cost and simple preparation [24–28]. Unfortunately, BVO also have similar problems with TiO₂ [29]. Although a variety of modification techniques, including noble metal deposition and composite semiconductor materials [30], have been adopted
to improve the photocatalytic activity, the high cost and complicated process limit the further promotion. However, Ion doping is indeed a convenient and cost-effective strategy to enhance the activity of photocatalysts, especially for transition metal ions due to their high earth abundance and obvious improvement effect.

To the best of our knowledge, the research on Ni-doped BiVO₄ (NBVO) removal for RhB has not been reported. Hence, we propose a simpler hydrothermal method with lower temperature to synthesize NBVO for decolorization of RhB. Simple process, green and low cost are more conducive to industrial implementation. Furthermore, the test of photoelectric performance provides powerful evidence for the improvement of NBVO photocatalytic activity. The capture experiments in this work identifies the active group of NBVO photocatalysis. Herein, the photocatalyst NBVO decontaminates organic dye wastewater as a novel attempt. This work provides a highly efficient photocatalyst for the practical application in removal of highly persistent NBVO.

2. Materials and methods

Analytical reagents purchased from Chengdu Kelong Chemical Ltd (Chengdu, China), including sodium hydroxide (NaOH), nitric acid (HNO₃), bismuth nitrate (Bi(NO₃)₃ · 5H₂O), absolute ethanol (CH₃CH₂OH), ammonium metavanadate (NH₄VO₃), nickel nitrate (Ni(NO₃)₂ · 6H₂O), ethylenediaminetetraacetic acid disodium (EDTA-2Na), isopropyl alcohol, 1,4-p-benzoquinone (BZQ) and Rhodamine B (C₂₈H₃₁ClN₂O₃). All experimental water was deionized water in this work.

2.1. Preparation of NBVO

NBVO was prepared using a facile hydrothermal method. Concretely synthesis, 2.5 mmol NH₄VO₃ and 2.5 mmol Bi(NO₃)₃ · 5H₂O were dissolved in 2 mol l⁻¹ NaOH solution and 2 mol l⁻¹ HNO₃ solution, respectively, and named as solution A and solution B in turn. After that, solution A was slowly added dropwise to solution B, and magnetically stirred for 60 min. Subsequently, the mixed solution was adjusted to pH = 10 by 1 mol l⁻¹ NaOH solution, and then sonicated for 10 min. Finally, the homogeneous mixed solution was poured into a Teflon-lined stainless-steel autoclave at 160 °C for 8 h. The synthesized BVO was washed with distilled water and absolute ethanol, and dried at 80 °C for 8 h. The obtained product was pure BVO. The key to NBVO preparation was that Ni(NO₃)₂ · 6H₂O with different mass ratios were added to solution B (theoretically generated mass ratio of BVO). Finally, the resulting solution B went through the remaining procedures of BVO preparation to harvest the target product NBVO. The schematic illustration of NBVO photocatalyst synthesis was shown in figure 1.

2.2. Characterization

The structures of the samples were examined by x-ray diffraction (XRD, XRD-6000, Shimadzu, Kyoto, Japan), Raman spectra (LabRAM HR, HORIBA, France) and Fourier transform infrared spectroscopy (FTIR, Nicolet iS50, Thermo Fisher Scientific Inc., China). The morphology and microstructure characterization were probed by a scanning electron microscope (SEM, QUANTA250, FEI Company, USA) with an energy-dispersive x-ray spectrometer (EDS). The optical properties were investigated by UV–vis diffuse reflectance spectrometer (UV–vis DRS, TU-1901, Persee, Beijing, China) equipped with a diffused integrated sphere. The chemical composition was analyzed by x-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Fisher Scientific Inc., USA).

Figure 1. The synthesis process of NBVO.
Scientific Inc., USA) with monochromatic Al Kα irradiation. Specific surface area and pore size distribution were determined by Brunauer–Emmett–Teller (BET, Quadrasorb 2MP, Quantachrome Instruments, USA).

2.3. Photocatalytic tests
The light source used a 300 W xenon lamp (CEL-HXF 300, Beijing CEAULIGHT Co., Ltd, Beijing, China) with a 400 nm cutoff filter to simulate visible light generation. The activity of the prepared photocatalyst was studied by decomposing RhB. In a typical decolorization test, 0.1 g of photocatalyst was put into 100 ml of RhB (10 mg l⁻¹) solution. Before the photocatalytic reaction, the system was processed in darkness for 30 min to achieve adsorption equilibrium and homogeneous dispersion. Under light conditions, 5 ml of the test sample was centrifuged every 15 min, and the centrifuged supernatant was taken to determine the absorbance. It was worth noting that all samples were tested 3 times and averaged. Finally, the decolorization rate of RhB was calculated using equation (1) [32]:

\[
\text{DR(\%)} = \left(1 - \frac{C}{C_0}\right) \times 100
\]  

(1)

Where DR represents the decolorization rate of RhB under visible light irradiation, \(C_0\) and \(C\) are the initial concentration and the concentration at \(t\) min, respectively.

2.4. Photoelectrochemical and electrochemical measurements
The photoelectrochemical test was carried out with electrochemical workstation (the CHI660E), and the test was carried out using the traditional three-electrode system. Taking Ag/AgCl as reference electrode and Pt sheet electrode as counter electrode, the fluorine-doped tin oxide (FTO) (working area of \(1 \times 1 \text{cm}^2\)) of the prepared catalyst was applied as working electrode [33]. The 0.5 mol l⁻¹ Na₂SO₄ solution was used as the electrolyte, and the visible light source was a 300 W Xe lamp light source with a filter. In this work, all the measured potentials were converted to reversible hydrogen electrodes (RHE) using the Nernst equation,

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \text{pH}
\]  

(2)

where \(E_{\text{RHE}}\) is the conversion potential relative to RHE, \(E_{\text{Ag/AgCl}}\) is the experimentally measured potential versus Ag/AgCl (saturated KCl solution).

3. Results and discussion

3.1. Characterization on the Structure and Specific Surface Property
Figure 2 shown the XRD spectrum of the BVO and NBVO photocatalytic material. The single peak of as-synthesized BVO had high intensity and good crystallinity. Besides, all the diffraction peaks of BVO were highly consistent with the monoclinic BVO standard diffraction card (JCPDS No. 14-0688). The lattice parameters of the monoclinic system BVO were \(a = 5.195 \text{ Å}, b = 11.701 \text{ Å}, c = 5.092 \text{ Å}, \alpha = \beta = 90^\circ, \gamma = 90.38^\circ\), and \(V = 309 \text{ Å}^3\). The main diffraction peaks of NBVO at \(2\theta = 18.7^\circ, 19.0^\circ, 28.9^\circ, 30.5^\circ, 34.5^\circ\) and \(35.2^\circ\) corresponded to the reflection from (011), (110), (121), (040), (200) and (002) crystal planes, respectively. In addition, 0.75% NBVO had higher crystallinity in the doped samples. Hence, 0.75% NBVO was used for the subsequent test. The characterization results expressed that the characteristic diffraction peaks of NBVO

![Figure 2](image-url)
remained the same as pure BVO, which proved that Ni doping had no effect on the composite sample. It can be seen from figure 2(b) that Ni will cause the diffraction peak to move toward a small angle, which may be caused by Ni ions entering the BVO crystal gap.

The crystallite size of BVO and NBVO was calculated using the Scherrer equation [32]:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

where, \(K\) is a dimensionless shape factor with a typical value of unity; \(\lambda\) is the x-ray wavelength of the employed XRD instrument in nm; \(\beta\) is the line broadening at full width at half maximum intensity (FWHM XRD) in radian; \(\theta\) is the Bragg angle in radian.

\(\beta\) was calculated using MDI Jade 6 software (the sharpest peaks as seen in figure 2) from the lower range of diffraction angles, i.e., (110), (011), (121), (040), (200) and (002) of BVO and NBVO with the above 6 crystal faces were selected as the representative peaks for this analysis. Finally, the crystallite sizes calculated from different samples were averaged, and the results are shown in table 1. The average grain size of BVO before and after being doped did not change significantly in table 1. At the same time, it was observed that the increase in Ni content did not cause the change in grain size.

Figure 3 was the FT-IR spectrum test results for 0.75% NBVO and BVO. 745 cm\(^{-1}\) and 833 cm\(^{-1}\) were the symmetric stretching vibration peak and the asymmetric stretching vibration peak of the V–O bond, respectively. The strong and broad absorption peaks at 1380 cm\(^{-1}\) and 3463 cm\(^{-1}\) may be due to the stretching vibration peaks of water molecules and hydroxyl groups adsorbed on the surface of the photocatalyst [34]. Interestingly, the characteristic diffraction peak of Ni was not found in figure 3, which may be attributed to Ni entering the 0.75% NBV lattice in the form of ions.

XPS was performed to identify the detailed chemical compositions and states of NBVO, and the measurement results were displayed in figure 4. It was confirmed in figure 4(a) that 0.75% NBVO had Bi, V, O, C and Ni elements. The appearance of the carbon signal could be ascribed to the test instrument. The characteristic peak of the binding energy around 855 eV was attributed to the peak of Ni\(^{3+}\). The lower intensity of the peak should be due to the low amount of doped Ni\(^{3+}\) [35]. As shown from figure 4(b), the XPS high-resolution peaks with binding energy at 872.8 eV and 855.7 eV were the signal peaks of Ni 2p\(_{1/2}\) and Ni 2p\(_{3/2}\), respectively. In addition, the XPS points with binding energy at 879.0 eV was assigned to the satellite peak of Ni 2p\(_{1/2}\), and the XPS sub-peak with the binding energy at 861.4 eV from the satellite peak of Ni 2p\(_{3/2}\). Therefore, the Ni element was present in the NBVO photocatalytic material. Figures 4(c)–(e) indicated the high-resolution XPS spectrums of V 2p, O 1s and Bi 4f, which denoted the attendance of V element in pent-valence state, Bi element in trivalent state and O element in bi-valence state, respectively [36]. It was worth noting that the XPS results were consistent with XRD, proved that BVO was successfully doped with Ni [37].

| Samples | BVO | 0.25% | 0.50% | 0.75% | 1.00% | 1.50% |
|---------|-----|-------|-------|-------|-------|-------|
| D (nm)  | 42.676 | 42.675 | 42.674 | 42.675 | 42.671 | 42.674 |

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Figure 3. FT-IR spectrum of BVO and 0.75% NBVO.
Figure 5 was the Raman characterization of BVO and 0.75% NBVO. The peak intensity values marked in the figure 5 were all caused by the vibration signal of V-O. Moreover, BVO and NBVO could correspond to each other well. This result directed that the incorporation of Ni ions did not change the structure of BVO. At the same time, the Raman outcomes also proved that BVO should be a stable substance. However, the peak intensity of the doped sample became weak, which may be due to the substitution of Ni for the stronger Bi\textsuperscript{38}. Above results collectively demonstrated the successful preparation of the doped specimen.

The surface morphology of the prepared photocatalysts was investigated by SEM images, illustrated in figure 6. As seen from figure 6, BVO were irregular particles, which appeared to be flakes after doping. The reason for the change in microscopic morphology may be the addition of nickel nitrate to the precursor of BVO, which promoted the morphology transformation of the doped materials. EDS was used to study whether Ni ions successfully entered the BVO crystal structure. EDS results displayed that 0.75% NBVO contained B, V, O, Ni and C elements. Among them, the appearance of carbon can be related to the test equipment. Additionally, the

Figure 4. XPS patterns of 0.75% NBVO: (a) XPS full patterns; (b) Ni 2p; (c) V 2p; (d) O 1s; (e) Bi 4f.
observation of Ni verified the successful preparation of NBVO. It was consistent with the characterization results of XRD, XPS and Raman.

Figure 7 shows the N2 adsorption-desorption isotherms and the pore size distributions (inset) of the as-prepared photocatalytic materials. It was distinctly observed that the curve of BVO was similar to that of NBVO. During the progress of adsorption, desorption was enhanced without hysteresis, which was a typical characteristic of the type III isotherm adsorption curve \[39, 40\]. As shown in table 2, the \(S_{BET}\) and the pore volume of 0.75% NBVO sample (33.8 m\(^2\) g\(^{-1}\) and 0.13 cm\(^3\) g\(^{-1}\)) were higher than that of BVO sample (24.5 m\(^2\) g\(^{-1}\) and 0.08 cm\(^3\) g\(^{-1}\)), which may be beneficial for enhancing the photocatalytic activities due to provide more reaction active sites during the photocatalytic reaction \[41, 42\]. In addition, it can be seen from the inset in figure 7 that the pore sizes of BVO and 0.75% NBVO were basically distributed in 3–10 nm, indicating that the as-synthesized both semiconductor photocatalysts were mesoporous materials.

3.2. UV–vis DRS

The optical absorption property of samples was characterized by UV–vis DRS. Figure 8 displayed the UV–vis DRS spectra of BVO and 0.75% NBVO. The BVO sample exhibited a narrower range of light absorption (565 nm), but the light absorption edge of 0.75% NBVO can be extended to 580 nm (figure 8). The band gap energy of BVO and 0.75% NBVO were 2.39 eV and 2.37 eV, respectively, and their band gap were not significantly different. Noteworthily, the band gap of Ni-doped materials was reduced and the absorption edge was red-shifted. As a result, it was beneficial to the photocatalytic activity of 0.75% NBVO.

3.3. Photocatalytic activity and reusability

The effect of 0.75% NBVO decomposing RhB under visible light illumination and UV–visible spectrum degradation variations were revealed in figure 9. The Ni-doped samples showed a much higher photocatalytic ability than BVO within 75 min (figure 7(a)). Correspondingly, the BVO degraded only 44% RhB at 75 min. Surprisingly, the photocatalyst with a theoretical doping amount of 0.75 wt% had the best decolorization effect (96%) on RhB. In addition, it was found that the decomposition rate did not increase with increasing doping amount in figure 7(a). Besides, the highest absorption peak of RhB was blue-shifted from the initial 554 nm to 500 nm (figure 9(b)), which indicated that RhB was degraded to small molecules due to deethylation reaction under visible light conditions. The decolorization of RhB conformed to the pseudo-first-order kinetic model, which was proved to be equation (3) \[43\]:

\[
\ln(C_0/C) = kt
\]

where \(C_0\) and \(C\) are the original concentration and the concentration at \(t\) min of RhB, and \(k\) represents the reaction rate constant. The kinetic linear fitting curves and rate constant values of the photocatalytic decolorization rate of RhB for different samples are shown in figures 9(c), (d), respectively. Herein, the \(k\) values of BVO and NBVO (0.25–1.5 wt%) were respectively 0.0073, 0.01587, 0.02159, 0.03928, 0.02176 and 0.0104 min\(^{-1}\). Dramatically, the first-order kinetic rate constant of 0.75% NBVO was about five times that of the pure BVO. Meanwhile, the rate constant values of NBVO with the addition of Ni had an interesting phenomenon of increasing first and then decreasing. Namely, the photocatalytic activity of 0.75% NBVO was the optimum compound ratio, which was suitable for further testing. The above results were consistent with the
0.75% NBVO selected in the XRD conclusions. Ultimately, the photocatalytic activity of this work was compared with similar doped BVO as shown in table 3. By comparison, it was found that both the similar doped BVO and the typical TiO₂, NBVO had a better decolorization effect for high concentration of RhB under low light energy and short reaction time.

The catalytic performance and structural stability of a photocatalyst are one of the important indicators for evaluating its practical value. So, 0.75% NBVO substances were reused to decontaminate simulated organic pollutant RhB under visible light irradiation, as shown in figure 10. After four reuse experiments, the...
decolorization efficiency of 0.75% NBVO for RhB decreased from the initial 96% to 86%. The experimental consequences declared that Ni doping could improve the stability and photo corrosion resistance of BVO. At the same time, it was further proved that 0.75% NBVO had an outstanding stability and long lifetime.

### 3.4. Photoelectric performance

The carrier mobility of BVO and 0.75% NBVO was measured by electrochemical impedance spectroscopy, and listed in figure 11. The impedance arc of BVO was greater than that of 0.75% NBVO, which meant that 0.75% NBVO had a faster migration rate of photogenerated carrier (figure 11). In the equivalent circuit diagram of figure 11, the equivalent values of $R_s$ and $R_{ct}$ of BVO were 27 $\Omega$ and 848 $\Omega$, respectively. Similarly, the equivalent values of 0.75% NBVO were 25 $\Omega$ and 322 $\Omega$. The resistance of the electrolyte tended to be stable, and the fitted $R_{ct}$ resistance value of 0.75% NBVO is smaller than that of BVO. These results evidenced that the enhanced

![Figure 7](image1.png)

**Figure 7.** The adsorption–desorption isotherms of BVO and 0.75% NBVO, illustrated with pore size distribution curve in the inset.

![Figure 8](image2.png)

**Figure 8.** UV–vis DRS spectra and corresponding band gap energy of BVO and 0.75% NBVO.

| Samples     | $S_{BET}$ area ($m^2 \cdot g^{-1}$) | Pore volume ($cm^3 \cdot g^{-1}$) | Pore size |
|-------------|-----------------------------------|-----------------------------------|-----------|
| BVO         | 24.5                              | 0.08                              | 4.24      |
| 0.75% NBVO | 33.8                              | 0.13                              | 3.35      |

Table 2. The specific surface area, pore volume and pore size of BVO and 0.75% NBVO.
mobility of photogenerated carriers may be caused by the reduced charge transfer resistance of 0.75% NBVO. Therefore, 0.75% NBVO exhibited better photocatalytic activity.[51]

By testing the instantaneous photocurrent density (I-t) of BVO and 0.75% NBVO, the electron migration rate of the samples were further verified[52]. Figure 12 revealed the instantaneous photocurrent density of BVO and 0.75% NBVO. From figure 12, The instantaneous photocurrent densities of BVO, 0.25% NBVO, 0.5% NBVO, 0.75% NBVO, 1.0% NBVO and 1.5% NBVO were 0.077 μA · cm⁻², 0.1 μA · cm⁻², 0.24 μA · cm⁻², 0.086 μA · cm⁻², and 0.05 μA · cm⁻², respectively. The instantaneous photocurrent density change value of the samples, which may be related to the sample’s energy gain under visible light irradiation, and the migration of electrons after being excited[53]. In addition, the instantaneous photocurrent density values of NBVO were consistent with the photocatalytic activity results, which again suggested that appropriate Ni could effectively improve the photocatalytic activity of BVO. Especially, the improvement of the I-t of 0.75% NBVO had the

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**Table 3. Comparing the photocatalytic activity of NBVO and the recently reported doped BVO photocatalysts to degrade RhB under visible light irradiation.**

| Catalysts          | Xenon lamp | Concentration | Volume | Mass of catalysts | Time | Removal rate | References |
|--------------------|------------|---------------|--------|-------------------|------|--------------|------------|
| Gd-doped BiVO₄     | 500 W      | 5 mg l⁻¹      | 50 ml  | 0.05 g            | 120 min | 96.0%        | [44]       |
| Br-doped BiVO₄     | 500 W      | 10 mg l⁻¹     | 50 ml  | 0.05 g            | 240 min | 78.9%        | [45]       |
| Nd-doped BiVO₄     | 500 W      | 5 mg l⁻¹      | 50 ml  | 0.05 g            | 120 min | 94.0%        | [46]       |
| Br-doped TiO₂      | 500 W      | 0.01 mol l⁻¹  | 50 ml  | 0.1 g             | 50 min  | 96.5%        | [47]       |
| Bi-doped TiO₂      | 500 W      | 1 x 10⁻³ mol l⁻¹ | 50 ml | 0.05 g            | 90 min  | 100.0%       | [48]       |
| Ni-doped TiO₂      | 220 W      | 10 mg l⁻¹     | 100 ml | 0.03 g            | 180 min | 57.0%        | [49]       |
| TiO₂               | 300 W      | 10 mg l⁻¹     | 50 ml  | 0.01 g            | 90 min  | 42.4%        | [50]       |
| BiVO₄              | 300 W      | 10 mg l⁻¹     | 100 ml | 0.1 g             | 75 min  | 44.0%        | This work  |
| Ni-doped BiVO₄     | 300 W      | 10 mg l⁻¹     | 100 ml | 0.1 g             | 75 min  | 96.0%        | This work  |

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Figure 9. (a) Photocatalytic decolorization rate of RhB by the as-prepared samples; (b) Time-dependent UV-vis spectra of RhB solution by the 0.75% NBVO; (c) First-order dynamics simulation curves of BVO and NBVO (0.25–1.5 wt%); (d) Kinetic rate constant values of BVO and NBVO (0.25–1.5 wt%).
Figure 10. Recycling tests on 0.75% NBVO for decolorization of RhB under visible light irradiation.

Figure 11. Electrochemical impedance spectroscopy of BVO and NBVO with equivalent circuit diagram ($R_s$ and $R_{ct}$ represent the resistance of the electrolyte and the resistance of the interface between the semiconductor and the electrolyte, respectively).

Figure 12. Transient photocurrent response of BVO and 0.75% NBVO.
superiority that the recombination rate of holes and electrons became lower. Based on the results, the excellent photocatalytic activity of 0.75% NBVO was confirmed on the other hand.

### 3.5. Decolorization mechanism

Photocatalysts can generate superoxide radicals (\( \cdot O_2^- \)), hydroxyl radicals (\( \cdot OH \)), photoelectrons \([54]\) and holes (\( h^+ \)) in decolorization reaction. Hence, in order to speculation the possible photocatalyst mechanism, EDTA-2Na, IPA and BZQ were used as trapping agents for \( h^+ \), \( \cdot OH \) and \( \cdot O_2^- \), respectively. Figure 13 showed the effect of 0.75% NBVO on the decolorization rate of RhB with the addition of different kinds and the same number of scavengers. All three capture agents had an effect on the photocatalytic activity of 0.75% NBVO (figure 13(a)). With the addition of EDTA-2Na, IPA and BZQ, the decolorization rates of RhB within 75 min by 0.75% NBVO were 97%, 94% and 43%, respectively (figure 13(b)). The experimental results presented that \( \cdot O_2^- \) was active substance in the process of photocatalytic reaction. On the basis of the above experimental results, plausible mechanism for photocatalytic decolorization of RhB by NBVO was shown in figure 14. First of all, when visible light was irradiated onto the surface of NBVO, the semiconductor was excited after absorbing light to generate electron-hole pairs. Secondly, the electrons in the valence band transited to the conduction band, and the carriers separated and migrated to NBVO surface. Doping Ni ions in the BVO lattice could form an electron capture center, resulting in a reduction in the recombination rate of electrons and holes \([55]\). Therefore, this is also one of the reasons why the doped samples improved the
photocatalytic activity. Eventually, electrons could interact with dissolved O₂ to generate strong oxidizing \( \cdot O_2^- \), so as to achieve the purpose of degrading wastewater [56]. Based on experimental analysis and literature researches, it was concluded that the reactions occurred during the decolorization of RhB by NBVO should follows:

\[
\text{NBVO} + h\nu \rightarrow h^+ + e^- \\
\text{Ni}^{2+} + h\nu \rightarrow \text{Ni}^{3+} + e^- \\
\text{Ni}^{3+} + e^- \rightarrow \text{Ni}^{2+} \\
O_2 + e^- \rightarrow \cdot O_2^- \\
\text{RhB} + \cdot O_2^- \rightarrow \text{Removal products}
\]

4. Conclusions

The photocatalyst NBVO with preeminent photocatalytic activity was prepared by a simple and undemanding hydrothermal method, which was applied to decompose the refractory organic dye RhB. XRD, EDS, XPS, FTIR and Raman spectroscopy confirmed that Ni was successfully doped into BVO. The NBVO photocatalytic activity had been stupendous improved. In particular, the 0.75% NBVO exhibited the upmost photocatalytic property, achieving 96% decolorization efficiency within 75 min under visible-light irradiation, which was due to the introduction of suitable Ni ions. The improved photoelectric performance of NBVO was also employed to explain the enhanced photocatalytic activity. On the one hand, 0.75% NBVO was a stable material, and the decolorization rate could still reach 86% after four cycles. On the other hand, the active radicals \( \cdot O_2^- \) play a crucial role in enhancing the photocatalytic performance, corresponding to the discussion of the scavengers trapping test. This work presents a simpler strategy to synthesize high efficiency visible-light-driven green photocatalyst. NBVO was used to treat organic wastewater RhB, which will be a new perspective for NBVO to handle wastewater. Simultaneously, NBVO has the opportunity to become the novel favorite of environmental remediation materials.

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Author contributions

Conceptualization, S L and Q W; Data curation, Y C and Q W; Methodology, S L and Q W; Resources, C L and L X; Writing, Y C; Writing—review and editing, S L, Y C, and Q W. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interest

The authors declare no conflicts of interest.

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References

[1] Lai Y-H, Palm D W and Reisner E 2015 Multifunctional coatings from scalable single source precursor chemistry in tandem photoelectrochemical water splitting Adv. Energy Mater. 5 1501668
[2] Hasan M K, Shahriar A and Jin K U 2019 Water pollution in Bangladesh and its impact on public health Heliyon 5 e02145
Li H-B, Zhang J, Huang G-Y, Fu S-H, Ma C, Wang B-Y, Huang Q-R and Liao H-W 2017 Hydrothermal synthesis and enhanced photocatalytic performance of BiVO4 and its activities of photocatalytic applications. J. Mater. Chem. 29, 10337-48

Tab A, Bellal B, Belahed C, Dahmane M and Trari M 2020 Visible light assisted photocatalytic degradation and mineralization of Rhodamine B in aqueous solution by Ag3PO4. ACS Appl. Mater. Interfaces 12, 19002-9

Patil C S, Kadam A N, Gunjal D B, Naik V M, Lee S-W, Kolekar G B and Gore A H 2020 Sugarcane molasses derived carbon sheet@sea sand composite for direct removal of methylene blue from textile wastewater: Industrial wastewater remediation through sustainable, greener, and scalable methodology. Sep. Purif. Technol. 247, 116997

Yang R, Cai J, Lv K, Wu X, Wang W, Xu Z, Li M, Li Q and Xu W 2017 Fabrication of TiO2 hollow microspheres assembly from TiO2 nanosheets. J. Photochem. Photobiol., A 377, 190-4.
[39] Wang R, Jin X, Wang Z, Gu W, Wei Z, Huang Y, Qiu Z and Jin P 2017 A multilevel reuse system with source separation process for printing and dyeing wastewater treatment: a case study Bioresour. Technol. 247 1233–41
[40] Lopes O, Carvalho K, Avansi W and Ribeiro C 2017 Growth of BiVO₄ nanoparticles on a Bi₂O₃ surface: effect of heterojunction formation on visible irradiation-driven catalytic performance J. Phys. Chem. C 121 13747–56
[41] Xing Y, Wang J, Chen L, Wang A, Li F, Wang C and Zhong E 2016 Synthesis and characterization of Cu–BiVO₄/MCM-41 composite catalysts with enhanced visible light photocatalytic activities J. Mater. Sci., Mater. Electron. 27 8633–40
[42] Lu Y, Xu L and Liu C 2019 Magnetically separable and recyclable photocatalyst MoS₂–SrFe₁₂O₁₉ with p-n heterojunction: Fabrication, characterization, and photocatalytic mechanism Appl. Organomet. Chem. 34 e5288
[43] Wang H, Xu L, Liu C, Jiang Z, Feng Q, Wu T and Wang R 2020 A novel magnetic photocatalyst Bi₂O₄Cl/SrFe₁₂O₁₉ fabrication, characterization and its photocatalytic activity Ceram. Int. 46 460–7
[44] Luo Y, Tan G, Dong G, Ren H and Xia A 2016 A comprehensive investigation of tetragonal Gd-doped BiVO₄ with enhanced photocatalytic performance under sun-light Appl. Surf. Sci. 364 156–65
[45] Qin C, Liao H, Rao F, Zhong J and Li J 2020 One-pot hydrothermal preparation of Br-doped BiVO₄ with enhanced visible-light photocatalytic activity Solid State Sci. 105 106285
[46] Luo Y, Tan G, Dong G, Ren H and Xia A 2015 Effects of structure, morphology, and up-conversion on Nd-doped BiVO₄ system with high photocatalytic activity Ceram. Int. 41 3259–68
[47] Wang Q, Zhu S, Liang Y, Cui Z, Yang X, Liang C and Inoue A 2017 One-step synthesis of size-controlled Br-doped TiO₂ nanoparticles with enhanced visible-light photocatalytic activity Mater. Res. Bull. 86 248–56
[48] Xu J, Wang W, Shang M, Gao E, Zhang Z and Ren J 2011 Electrospun nanofibers of Bi-doped TiO₂ with high photocatalytic activity under visible light irradiation J. Hazard. Mater. 196 426–30
[49] Pol R, Guerrero M, García-Lecina E, Altube A, Rossinyol E, Garroni S, Baró M D, Pons J, Sort J and Pellicer E 2016 Ni-, Pt- and (Ni/Pt)-doped TiO₂ nanophotocatalysts: a smart approach for sustainable degradation of Rhodamine B dye Appl. Catalysis B 181 270–8
[50] Sun X, Yan L, Xu R, Xu M and Zhu Y 2019 Surface modification of TiO₂ with polydopamine and its effect on photocatalytic degradation mechanism Colloids Surf., A 570 199–209
[51] Pan Q, Yang K, Wang G, Li D, Sun J, Yang B, Zhou Z, Hu W, Wen K and Yang H 2019 BiVO₄ nanocrystals with controllable oxygen vacancies induced by Zn-doping coupled with graphene quantum dots for enhanced photoelectrochemical water splitting Chem. Eng. J. 372 399–407
[52] Jia Y, Wang Z, Ma Y, Liu J, Shi W, Lin Y, Hu X and Zhang K 2019 Boosting interfacial charge migration of TiO₂/BiVO₄ photoanode by W doping for photoelectrochemical water splitting Electrochim. Acta 300 138–44
[53] Antuch M, Millert P, Iwase A and Kudo A 2018 The role of surface states during photocurrent switching: intensity modulated photocurrent spectroscopy analysis of BiVO₄ photoelectrodes Applied Catalysis B-Environmental 237 401–8
[54] Ruiz-Serrano D, Flores-Acosta M, Conde-Barajas E, Ramirez-Rosas D, Yañez-Limón J M and Ramirez-Bon R 2010 Study by XPS of different conditioning processes to improve the cation exchange in clinoptilolite J. Mol. Struct. 980 149–55
[55] Yulin H, Yongjin L, Yanchun X, Shenghong Y and Yueli Z 2020 Preparation and photocatalytic properties of bismuth ferrite nanopowder doped with Ni Materials Reports 18 18009–13
[56] Zhang Y, Yi Z, Wu G and Shen Q 2016 Novel Y doped BiVO₄ thin film electrodes for enhanced photoelectric and photocatalytic performance J. Photochem. Photobiol., A 327 25–32