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Mediator-Free Direct Z-scheme Photocatalytic System: BiVO$_4$/g-C$_3$N$_4$ Organic-Inorganic Hybrid Photocatalyst with Highly Efficient Visible-Light-Induced Photocatalytic Activity

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We disclose the fabrication of a mediator-free direct Z-scheme photocatalyst system BiVO$_4$/g-C$_3$N$_4$ by using a mixed-calcination method based on more reliable interfacial interaction. The facet coupling occurred between the g-C$_3$N$_4$ (002) and BiVO$_4$ (121) was revealed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscope (TEM). The crystal structure and optical property of the as-prepared samples have also been characterized by fourier-transform infrared (FTIR), scanning electron microscopy (SEM) and UV-vis diffuse reflectance spectra (DRS) in details. The photocatalytic experiments indicated that the BiVO$_4$/g-C$_3$N$_4$ composite photocatalysts display a significantly enhanced photocatalytic activity pertaining to RhB degradation and photocurrent generation (PC) compared to the pristine BiVO$_4$ and g-C$_3$N$_4$. This remarkably improved photocatalytic performance should be attributed to the fabrication of a direct Z-scheme system of BiVO$_4$/g-C$_3$N$_4$, which can result in a more efficient separation of photoinduced charge carriers than band-band transfer, thus endowing it with the much more powerful oxidation and reduction capability, as confirmed by the photoluminescence (PL) spectra and electrochemical impedance spectra (EIS). The Z-scheme mechanism of BiVO$_4$/g-C$_3$N$_4$ heterostructure was verified by a series of combined techniques, including the active species trapping experiments, NBT transformation and terephthalic acid photoluminescence probing technique (TA-PL) over BiVO$_4$/g-C$_3$N$_4$ composites and the pristine samples. The present work not only furthered the understanding of mediator-free Z-scheme photocatalysis, but also shed new light on the design of heterostructural photocatalysts with high-performance.

1. Introduction

As a green and potential technology, semiconductor photocatalysis plays a vital role in the aspects of environmental protection and solar energy conversion.\textsuperscript{1-7} Numerous attention have been paid toward the design of novel visible-light-responsive photocatalysts so as to maximize the utilization of the natural sunlight in the visible region ($\lambda > 420$ nm), which accounts for the largest proportion of the solar spectrum.\textsuperscript{8}

Construction of heterostructures between two semiconductors is considered to be an effective method to promote the photocatalytic activity. Nowadays, the Z-scheme principled photocatalyst has attracted considerable attention due to its much stronger redox capacity than band-band transfer photocatalyst.\textsuperscript{9}

The more negative CB and more positive VB potentials in Z-scheme photocatalyst separately endow the photogenerated electrons and holes with strong reduction and oxidation ability, thereby exhibiting significantly improved photocatalytic performance than the single component.\textsuperscript{5,9} For instance, the photocatalytic activity through the direct Z-scheme principle transfer is obviously higher than that by band-band transfer mechanism in the visible-light-responsive Ag@AgBr/g-C$_3$N$_4$ composite photocatalyst.\textsuperscript{7} Other Z-scheme photocatalysts also largely prolong the lifetime of photoexcited carriers and exhibit highly enhanced photocatalytic activity than the two individuals. The Z-scheme systems are usually obtained by coupling two different photocatalysts combined with an appropriate intermediate or mediator (e.g. noble metals Ag and Au),\textsuperscript{10-13} which suffer from many drawbacks, such as low stability, high cost, etc. Compared with the mediator-containing ternary Z-scheme system, the mediator-free direct Z-scheme photocatalytic system only consisting of two components exhibits high stability, economic feasibility, etc, thus possessing the more promising practical application.\textsuperscript{14-17}

As a promising candidate photocatalyst for organic pollutant removal and hydrogen production, graphite-like carbon nitride (g-C$_3$N$_4$) exhibits relatively high photocatalytic activity under visible-light irradiation due to its rapid separation of photoinduced charge carriers.\textsuperscript{18-20} The very negative conduction band (-1.13 eV) of g-C$_3$N$_4$ enables a strong reduction power of the electrons (e') in the conduction band (CB). Nevertheless,
there are still some shortcomings for the g-C₃N₄ utilization in photocatalysis process, such as the limited visible-light absorption below 450 nm, and small specific surface area.²¹,²² Recently, continuous efforts have been made to improve the photocatalytic performance of g-C₃N₄. Among which, combining g-C₃N₄ with other appropriate semiconductors to construct heterostructures can effectively promote the separation rate of photoexcited charge carriers. BiVO₄ is a visible-light-responsive photocatalyst with a narrow band gap of 2.40 eV, which has been admitted as a potential visible-light photocatalyst.²³,²⁵ However, the photogenerated e⁻ and h⁺ can be quickly decay via recombination,²⁶ resulting in relatively low photocatalytic activity of BiVO₄. Therefore, it limits the practical applications of BiVO₄ in photocatalytic degradation of pollutants. Consequently, it is an urgent strategy to enhance the efficiency of charge carries separation rate and improve the visible-light photocatalytic activity of BiVO₄.

After energy level analysis, we found that the gap between the CB of g-C₃N₄ and the CB of BiVO₄ is much larger than that between the CB of BiVO₄ and the VB of g-C₃N₄. It may lead to that the photoinduced electrons in the CB of BiVO₄ transfer to the VB of g-C₃N₄ rapidly, which leaves rich electrons in the CB of g-C₃N₄ and holes in the VB of BiVO₄ to participate in the redox process, thus may result in a mediator-free direct Z-scheme photocatalytic system. Herein, we successfully prepared the direct Z-scheme photocatalyst system of BiVO₄/g-C₃N₄ by employing a mixed-calcination method, which may provide a more strong and reliable interfacial interaction between g-C₃N₄ and BiVO₄. The coupling between g-C₃N₄ and BiVO₄ happens on the (002) and (121) facets of g-C₃N₄ and BiVO₄ respectively. The photochemical activity of the BiVO₄/g-C₃N₄ was monitored via photocatalytic decomposition of the Rhodamine B (RhB) and photocurrent generation under visible-light irradiation (λ > 420 nm). The direct Z-scheme system of BiVO₄/g-C₃N₄ leads to a high efficiency separation of photogenerated electrons and holes, thus a highly improved photocatalytic activity. It was demonstrated by the active species trapping experiments, NBT transformation and terephthalic acid photoluminescence probing technique (TA-PL). It will be a generalized strategy to design other mediator-free direct Z-scheme photocatalysts with high-performance.

2. Experimental Section

2.1 Synthesis of heterostructured BiVO₄/g-C₃N₄ photocatalyst

The chemicals used in this study were of analytical grade without further purification. The g-C₃N₄ was synthesized via a calcination treatment of 5 g melamine in a corundum crucible without a cover in nitrogen.²³,²⁶ The crucible containing melamine was put into tube furnace and heated at 520°C for 4h. After cooling to room temperature, the yellow g-C₃N₄ product was obtained.

Pure BiVO₄ was prepared by a hydrothermal method as following. First of all, 0.005 mol of Bi(NO₃)₃·5H₂O was completely dissolved in 20 mL of HNO₃ (2 M) to form solution A. Second, 0.005 mol of NH₄VO₃ was dissolved in 10 mL of 2 M NaOH solution to form solution B. Then, solution B was dropwise added into solution A to form a yellow mixture.

The BiVO₄/g-C₃N₄ composites were obtained according to the following procedure. In a typical synthesis of BiVO₄/g-C₃N₄ with the molar ratio 1:9, 0.009 mol of g-C₃N₄ and 0.001 mol of BiVO₄ were mixed and ground thoroughly for 5 min. After that, the mixture was calcined at 400°C for 4 h to obtain the 1:9 BiVO₄/g-C₃N₄ photocatalyst. Other BiVO₄/g-C₃N₄ photocatalysts (2:8, 3:7, 4:6, 5:5 BiVO₄/g-C₃N₄) were prepared by the same processes, only the molar ratio of BiVO₄ to g-C₃N₄ were different. The pristine BiVO₄ and g-C₃N₄ were handled by the same method to ensure that they are under the same conditions.

2.2 Characterization

X-ray diffraction (XRD) analysis was employed to evaluate the phase structure of the as-prepared photocatalysts on a XRD-3 powder diffraction instrument with monochromatized Cu Kα radiation (λ= 1.5406 nm) at a setting of 40 kV and 40 mA, and the scanning range was 0.02° (2θ)/s and 10-70°, respectively. A Bruker spectrometer was used to achieve the fourier-transform infrared (FTIR) spectra at a frequency range of 4000-500 cm⁻¹. Scanning electron microscopy (SEM) on a FEI Quanta 250 FEG instrument was applied to examine the general morphology of the photocatalysts. And a S-4300 transmission electron microscope (TEM, Hitachi) was employed to obtain the morphology and microstructure. The specific surface area was collected from Brunauer-Emmett-Teller (BET) method by N₂ adsorption (ASAP 2460, Micromeritics, USA). UV-vis diffuse reflectance spectra (DRS) of the samples were recorded on a Cary 5000 (America Varian) spectrophotometer. The surface properties of the photocatalysts were obtained by X-ray photoelectron spectroscopy (XPS) on a Thermo ESCALAB 250 instrument (USA) operating at 150 W with Al Kα X-ray irradiation. The photoluminescence (PL) spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer to investigate the recombination rate of electrons and holes.

2.3 Photocatalytic evaluation

As a common organic pollutant, RhB was employed to evaluate the photocatalytic activities of the as-prepared photocatalysts under visible-light (λ > 420 nm) degradation illuminated by a 500 W xenon lamp. 50 mg of the powder photocatalysts were dropped into quartz tubes which were containing 50 mL of RhB solution (1×10⁻⁵ mol/L), respectively. Then, the above solution was ultrasonic dispersion for 10 min and stirred for 30 min in dark to achieve an adsorption-desorption equilibrium between the photocatalyst powder and RhB. Turn on the light and the photocatalytic reaction systems were exposed to visible light irradiation. At the same intervals, 3 mL of the mixture were taken out to centrifuge tubes, and the catalysts were removed out of the suspensions (4500 r/min, 5 min). The centrifuged solution was analyzed by recording the maximum absorption band (554 nm)
and UV-vis spectra were recorded by Shimadzu UV-5500PC spectrophotometer (produced by Shanghai Wuxiang Company).

2.4 Active species trapping and •O$_2^-$ and •OH quantification experiments

Tert-butyl alcohol (TBA), 1, 4-benzoquinone (BQ) and disodium ethylenediaminetetraacetate (EDTA) were added in order to investigate the main active species, such as hydroxyl radicals (•OH), superoxide radical (•O$_2^-$) and holes (h$^+$) produced during the photoreaction process.$^{10,27,28}$ NBT$^{17}$ (2.5 × 10$^{-9}$ mol/L) was used to detect the amount of •O$_2^-$ generated from g-C$_3$N$_4$, BiVO$_4$, 3:7 BiVO$_4$/g-C$_3$N$_4$ and mechanically mixed 3:7 BiVO$_4$/g-C$_3$N$_4$. The production of •O$_2^-$ was quantitatively analyzed by detecting the concentration of NBT with Shimadzu UV-5500PC spectrophotometer. To determine the amount of •OH producing from g-C$_3$N$_4$, BiVO$_4$, 3:7 BiVO$_4$/g-C$_3$N$_4$ and mechanically mixed 3:7 BiVO$_4$/g-C$_3$N$_4$ TA$^{29,30}$ (5 × 10$^{-4}$ M in a 2 × 10$^{-3}$ M NaOH solution) was used as a probe molecule to react with •OH generating a highly fluorescent product 2-hydroxymethylphosphinic acid, whose concentration can reflect the yield of •OH measured by a Hitachi F-4600 fluorescence spectrophotometer.

2.5 Photoelectrochemical measurements experiments

The photoelectrochemical experiments, including photocurrent response and electrochemical impedance spectra (EIS) of the samples as visible-light on and off, were conducted on a CHI660C electrochemical workstation (Chenhua Instrument Corporation, Shanghai). The BiVO$_4$/g-C$_3$N$_4$ film electrodes on ITO served as the working electrode, while a platinum maturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. A xenon lamp with a power of 500 W acted as visible-light source, and 0.1 M Na$_2$SO$_4$ was used as the supporting electrolyte. The working voltage of the BiVO$_4$/g-C$_3$N$_4$ electrode was 0 V. And the whole process of the measurement was conducted in air at room temperature.

3. Results and discussion

3.1. Characterization

XRD analysis was applied to survey and evaluate the phase structure of the samples. Fig. 1a shows the XRD patterns of g-C$_3$N$_4$, BiVO$_4$ and BiVO$_4$/g-C$_3$N$_4$ with different molar ratios. For the pure g-C$_3$N$_4$, it can be clearly seen that the two distinct diffraction peaks at 27.40° and 13.04° correspond to the (002) and (100) diffraction planes, respectively, revealing that the diffraction peaks of g-C$_3$N$_4$ were in good agreement with the tetragonal phase of g-C$_3$N$_4$ (JCPDS 87-1526).$^{3,12}$ Pure BiVO$_4$ shows a series of narrow and sharp diffraction peaks, which can be identified as the monoclinic phase of BiVO$_4$ (JCPDS 14-0688).$^{3,34}$ For BiVO$_4$/g-C$_3$N$_4$ samples, it can be observed that the characteristic peaks of g-C$_3$N$_4$ gradually appeared with the increase of the g-C$_3$N$_4$ content. Thus, the XRD patterns of BiVO$_4$/g-C$_3$N$_4$ samples demonstrated that the characteristic diffraction peaks consisted of both g-C$_3$N$_4$ and BiVO$_4$, reflecting existence of the two phases.

Fig. 1b shows the FTIR spectra of g-C$_3$N$_4$, BiVO$_4$ and BiVO$_4$/g-C$_3$N$_4$ composites. In the spectrum of pure BiVO$_4$, the peak at 742 cm$^{-1}$ can be attributed to the v$_3$ asymmetric stretching vibration of the VO$_4$ unit v$_3$ (VO$_4$), and that at 842 cm$^{-1}$ corresponded to the v$_1$ symmetric stretching vibration of the VO$_4$ unit v$_1$ (VO$_4$).$^{35,36}$ The absorption bands of pure g-C$_3$N$_4$ sample indicated the typical molecular structure of g-C$_3$N$_4$. The intense bands in 900–1200 cm$^{-1}$ region can be assigned to the typical stretching modes of CN heterocyclic. The intense band at 807 cm$^{-1}$ represented the out of plane breathing vibration characteristic of triazine units.$^{37,38}$ And the peak at 3430 cm$^{-1}$ was attributed to the existence of water. For the BiVO$_4$/g-C$_3$N$_4$ composites, the peak intensities of v$_1$ (VO$_4$) and v$_1$ (VO$_4$) increased slightly with the increase of BiVO$_4$ content, indicating the co-existence of g-C$_3$N$_4$ and BiVO$_4$ in the composites.

The morphology of g-C$_3$N$_4$, BiVO$_4$ and 3:7 BiVO$_4$/g-C$_3$N$_4$ were investigated by SEM. From Fig. S1a, a structure with several stacking layers could be clearly seen in the g-C$_3$N$_4$ sample, which was in line with the literature reports.$^{39,40}$ The BiVO$_4$ sample displayed a plate-like structure with a diameter of 50 ~ 200 nm and a thickness of 10 ~ 30 nm (Fig. S1b). Fig. S1c revealed that the two types of materials were all found in the sample of BiVO$_4$/g-C$_3$N$_4$ with the molar ratio of 3:7. In addition, it was observed that quantities of BiVO$_4$ nanoparticles were clustered on or covered by the g-C$_3$N$_4$ nanosheets. In addition, the EDS profile in Fig. S1d and e clearly verified the presence of Bi, V, O, C, N elements in the 3:7 BiVO$_4$/g-C$_3$N$_4$ composite. The signal of Au was due to the gilding process.

The microstructure of g-C$_3$N$_4$, BiVO$_4$ and 3:7 BiVO$_4$/g-C$_3$N$_4$ were further investigated by TEM and HRTEM. Clearly, the two-dimensional layered structure of the pure g-C$_3$N$_4$ can be seen from Fig. 2a. Based on the crystal structure of g-C$_3$N$_4$ from theoretical and previously experimental work, it might be inferred that the top surface of the layer is the (002) facet of g-C$_3$N$_4$ as presented in Fig. 2d. As shown in Fig. 2b, the pure BiVO$_4$ shows a number of plate-like nanostructures with a thickness of 10 ~ 30 nm. Also, Fig. 2b and HRTEM (Fig. 2e) proved that the top surface of BiVO$_4$ is (121) facet. Fig. 2c displayed the two type of nanosheets attached to each other with (002) facets of g-C$_3$N$_4$ and (121) facets of BiVO$_4$, indicating that the coupling between g-C$_3$N$_4$ and BiVO$_4$ may happen on the (002) facets of g-C$_3$N$_4$ and (121) facets of BiVO$_4$.

The XPS was employed to evaluate the surface chemical composition and the oxidation state of BiVO$_4$/g-C$_3$N$_4$ composites and to further study the interaction of g-C$_3$N$_4$ with BiVO$_4$. The overall XPS spectrum for the 3:7 BiVO$_4$/g-C$_3$N$_4$ was displayed in Fig. 3a, in which the Bi, O, V, C and N elements could be all investigated. Fig. 3b-f showed the high resolution spectra of Bi 4f, V 2p, O 1s, C 1s and N 1s for 3:7 BiVO$_4$/g-C$_3$N$_4$ composites, respectively. As shown in Fig. 3b, the binding energy values of Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ were observed at 164.4 eV and 159.1 eV, respectively. The high-resolution XPS spectra of 3:7 BiVO$_4$/g-C$_3$N$_4$ in Fig. 3c showed a peak at 529.5 eV, which can be attributed to V 2p. Obviously, two peaks can be detected in the high-resolution XPS spectra of O 1s region (Fig. 3d). And the main peak at 529.7 eV is assigned to the Bi-O bonds of (Bi$_2$O$_5$)$_{2+}$ slabs in the layered structure of BiVO$_4$, while the peak at 530.7 eV is ascribed to the hydroxyl groups on the surface.$^{41}$ In Fig. 3e, the peak of C 1s at 284.6 eV is the characteristic of the
adventicious carbon on the surface of g-C$_3$N$_4$ and the peaks at 286 eV and 288.2 eV were both attributed to the sp$^2$ hybridized C (C-(N$_i$)). The main features of N 1s are shown in Fig. 3f and a broad and wide peak (397 ~ 403 eV) can be seen. The existence of sp$^2$-bonded g-C$_3$N$_4$ in the BiVO$_4$/g-C$_3$N$_4$ composites could be verified by the N 1s peak at 398.8 eV reflecting the sp$^2$-hybridized nitrogen (C=N-C). The two peaks occurred at 400.1 eV and 401.3 eV were assigned to tertiary nitrogen (N-(C$_3$)) and the effects of charging reaction, respectively. The XPS results further demonstrated that the BiVO$_4$/g-C$_3$N$_4$ composite was successfully obtained.

The UV-vis DRS of the composites were displayed in Fig. 4, from which the optical absorption edges of the pure g-C$_3$N$_4$ and BiVO$_4$ were approximately estimated from the absorption onsets to be 450 and 525 nm, respectively. After the combination of g-C$_3$N$_4$ and BiVO$_4$, the absorption band edges of the composites gradually shift toward that of pure BiVO$_4$ with the increase of BiVO$_4$ content, which reveals that BiVO$_4$ is a good and appropriate visible-light sensitizer to g-C$_3$N$_4$. The band gap (E$_g$) can be determined by the formula:

$$\alpha h\nu = A (h\nu - E_g)^n$$

Where $\alpha$, $h$, m, $E_g$ and A are absorption coefficient, Planck constant, light frequency, band gap energy, and a constant, respectively. Among them, n is determined by the type of optical transition of a semiconductor (n = 1 for direct transition and n = 4 for indirect transition). As the previous literature reported, the n value of g-C$_3$N$_4$ was 4, and the n value of BiVO$_4$ was 1. From the plot of (ah$\nu$)$^{1/2}$ or (ah$\nu$)$^{2}$ versus (h$\nu$) in Fig. 4a and Fig. 4b, the $E_g$ of g-C$_3$N$_4$ and BiVO$_4$ were estimated to be 2.60 eV and 2.45 eV, respectively. Meanwhile, the $E_g$ of BiVO$_4$/g-C$_3$N$_4$ heterostructures were similar to that of pure BiVO$_4$.

3.2. Photocatalytic activity

The photocatalytic activity of the BiVO$_4$/g-C$_3$N$_4$ composite photocatalysts as well as pure BiVO$_4$ and g-C$_3$N$_4$ were examined by degradation of RhB molecules under visible-light irradiation ($\lambda > 420$ nm). Fig. 5a shows the photocatalytic degradation curves of RhB with the as-obtained photocatalysts under visible-light illumination for 5 h. It can be seen clearly that both the pristine g-C$_3$N$_4$ and BiVO$_4$ display relatively poor visible-light-induced degradation efficiency. When the molar ratio of BiVO$_4$ to g-C$_3$N$_4$ in the composites was 3:7, the highest degradation efficiency of 85% was observed within 5 h. The pseudo-first-order kinetic curves of RhB photodegradation were also plotted to analyze the degradation rate quantitatively. The experimental data clearly displayed that the apparent rate constant k is 0.033 h$^{-1}$, 0.032 h$^{-1}$, 0.066 h$^{-1}$, 0.139 h$^{-1}$, 0.342 h$^{-1}$, 0.041h$^{-1}$, and 0.049h$^{-1}$ for the pristine g-C$_3$N$_4$, BiVO$_4$ and BiVO$_4$/g-C$_3$N$_4$ composites with molar ratios of 1:9, 2:8, 3:7, 4:6, 5:5, respectively (Fig. 5c). In other words, the photocatalytic activity of 3:7 BiVO$_4$/g-C$_3$N$_4$ is 10.36 and 10.68 times higher than those of single g-C$_3$N$_4$ and BiVO$_4$, respectively. From Fig. 5b, the maximum absorbance of the solution shifted from 554 to 530 nm after 5 h irradiation, indicating that the N-demethylation and de-ethylation reactions happened during the photodegradation process. For the purpose of verifying the active species during the photocatalytic reaction and determining the corresponding photocatalytic mechanism, the tert-butyl alcohol (TBA), disodium ethylenediaminetetraacetate (EDTA) and 1, 4-benzoquinone (BQ) were employed as the hydroxyl radical (•OH) scavenger, hole (h$^+$) scavenger and superoxide radical (•O$_2^-$) scavenger, respectively. When EDTA was added to the solution, the RhB degradation rate for the 3:7 BiVO$_4$/g-C$_3$N$_4$ composite is slightly depressed as depicted in Fig. 5d, revealing that only a small amount of the holes were participated in the RhB degradation processes. However, the decrease of degradation rate is obviously observed with the addition of 1 mM of tertbutyl alcohol (TBA), which acted as a scavenger for •OH radical species. In addition, the degradation of RhB was also significantly depressed with adding 1 mM of •O$_2^-$ scavenger BQ, indicating that the •O$_2^-$ also play a vital role during the RhB oxidation process. Thus, the active species trapping experiments demonstrated that the •O$_2^-$ and •OH are the two main active species in the degradation process of RhB. For the sake of comparison, the influences of additions (EDTA, TBA and BQ) toward the photocatalytic activity over both pure BiVO$_4$ and g-C$_3$N$_4$ were also investigated as illustrated in Fig. S2. From Fig. S2, we can conclude that •O$_2^-$ plays the most crucial role in the oxidation process of RhB over pure g-C$_3$N$_4$. While for the pure BiVO$_4$, h$^+$ was the main active species in the RhB degradation process. Comparatively, as depicted in the Fig. 5d, the main active species of 3:7 BiVO$_4$/g-C$_3$N$_4$ sample in the degradation process of RhB are •O$_2^-$ and •OH, which was in agreement with the principle of Z-scheme photocatalytic mechanism. The BET specific surface area of 3:7 BiVO$_4$/g-C$_3$N$_4$ composite is 4.52 m$^2$/g, which is a little higher than bulk g-C$_3$N$_4$ (4.01 m$^2$/g), indicating that the slightly increased specific surface area is not the main reason for the highly enhanced photocatalytic activity of BiVO$_4$/g-C$_3$N$_4$ composite.

3.3. Mechanism investigation on the enhanced photocatalytic activity

The conduction band (CB) and valence band (VB) potentials of g-C$_3$N$_4$ and BiVO$_4$ can be calculated by the following equations:

$$E_{CB} = X - E_g + 0.5E_g$$

$$E_{VB} = X + 0.5E_g$$

where $E_{CB}$ is the VB edge potential; X is the electronegativity of the semiconductor, which is the geometric average of the absolute electronegativity of the constituent atoms (X values of g-C$_3$N$_4$ and BiVO$_4$ are 4.67eV and 6.16eV, respectively); $E_g$ is the energy of free electrons on the hydrogen scale ($E_z$ ≈ 4.5 eV); and $E_g$ is the band gap energy of the semiconductor. The band gap energies of g-C$_3$N$_4$ and BiVO$_4$ are adopted as 2.60 eV and 2.45 eV, respectively. The positions of the conduction and the valence bands of g-C$_3$N$_4$ and BiVO$_4$ calculated by Eq. (2) and (3) were listed in Table S1 (Supporting Information).

Fig. 6a depicts the crystal structure of BiVO$_4$, which is a typical scheelite compound. Its crystal structure is composed of alternating (Bi$_2$O$_5$)$_{6}^{3-}$ slabs and (VO$_2$)$_{6}^{3-}$ octahedral layers. This layered configuration is considered to enhance the separation of electron-hole pairs and decrease the recombination rate of the charge carriers. The (121) facet of BiVO$_4$ was figuratively marked in the Fig. 6a. The two types of nanosheets attached to
each other with (002) facets of g-C3N4 and (121) facets of BiVO4. Thus, we can deem that the coupled structure between g-C3N4 and BiVO4 will benefit for the separation of electron-hole pairs, so as to contribute to the enhancement of photodegradation on RhB under visible-light irradiation. The possible separation and transfer mechanism of the photoexcited charge carriers was proposed as depicted in Fig. 6c. Because the gap (1.56eV) between the CB of g-C3N4 and the CB of BiVO4 is much larger than that (1.04eV) between the CB of BiVO4 and the VB of g-C3N4, the photoexcited electrons in the CB of BiVO4 transfer to the VB of g-C3N4 quickly, leading to the combination of electrons in the CB of BiVO4 and photogenerated holes in the VB of g-C3N4. It accumulated rich electrons in the CB of g-C3N4 and holes in the VB of BiVO4 to involve in the redox reactions. Consequently, the more negative potentiated electrons in the CB of g-C3N4 reduce the molecular oxygen to yield \( \text{O}_2^- \), and then induces the RhB degradation. Meanwhile, the more positive potentiated holes in the VB of BiVO4 produce rich active \( \text{OH} \) radicals with powerful oxidation. Hence the photocatalytic activity of BiVO4/g-C3N4 composites were significantly promoted, and RhB is photodegraded via \( \text{O}_2^- \), \( \text{OH} \) or direct \( h^+ \) oxidation pathway. Based on the above results, the BiVO4/g-C3N4 system is a type of direct Z-scheme photocatalyst.

In order to prove the mechanism responsible for the remarkably improved visible-light induced photocatalysis, we conducted a series of tests such as photoluminescence spectra (PL), photocurrent-time measurement and electrochemical impedance spectroscopy (EIS).

PL emission mainly originated from the recombination of the photoexcited electrons and holes in semiconductors. And PL intensity has a strong correlation with photocatalytic activity of a photocatalyst. Generally, lower PL intensity reveals lower recombination rate of electron-hole pairs, thus higher photocatalytic performance.

In order to analyze the recombination of the charge carriers generated from g-C3N4, BiVO4, and 3:7 BiVO4/g-C3N4, the PL spectra with excitation wavelength 254 nm were measured and depicted in Fig. 7. The main emission peak centred on 460 nm for the g-C3N4 sample could be attributed to the band gap recombination of charge carriers. In comparison with g-C3N4, combining with BiVO4 does not affect the spectral position of the peaks, but reduces the relative intensity of PL spectra (inset of the Fig. 7). These results indicated that the mediator-free direct Z-scheme photocatalytic system of BiVO4/g-C3N4 dedicates to the effective charge separation, thus creating a significantly improved photocatalytic activity for the BiVO4/g-C3N4 composites under visible-light irradiation.

The photocurrent-time measurement was employed to evaluate the interfacial charge transfer dynamics between the g-C3N4 and BiVO4. Fig. 8a displays the transient photocurrent responses produced by the pure g-C3N4, BiVO4 and 3:7 BiVO4/g-C3N4 samples. The photocurrent intensity remained at a relatively high constant value when the light was on and rapidly decreased to zero as long as the light was turned off. Obviously, the photocurrent over 3:7 BiVO4/g-C3N4 composite is greatly improved, which is about 2 and 3 times as those of BiVO4 and g-C3N4, respectively. The higher photocurrent demonstrates the higher efficiency of charge separation. The results of photocurrent-time measurement suggested that the 3:7 BiVO4/g-C3N4 heterostructure possesses more powerful ability in charge separation than the pristine g-C3N4 and BiVO4. EIS measurement was employed to detect the charge transfer processes at solid/electrolyte interfaces. The radius of the arc on the EIS spectra implies the interface layer resistance happened on the surface of electrode. The smaller arc radius indicates the higher efficiency of charge transfer. As shown in Fig. 8b, the diameter of the arc radius on the EIS Nynquist plot of the 3:7 BiVO4/g-C3N4 composite electrode is much smaller than that of the pure BiVO4 electrode, suggesting a more effective separation of photoexcited charge carries and rapid interfacial charge transfer occurred in the 3:7 BiVO4/g-C3N4 composites.

To further confirm the Z-scheme mechanism and examine that the \( \text{O}_2^- \) and \( \text{OH} \) radicals mainly conduce to the degradation of RhB molecules over 3:7 BiVO4/g-C3N4 under visible light irradiation (\( \lambda > 420 \) nm). Qualification experiments of \( \text{O}_2^- \) production were performed thorough the transformation of NBT (detection agent of \( \text{O}_2^- \)) during the photocatalytic reaction. Fig. 9 showed the spectra of the transformation percentage of NBT. For pure g-C3N4, the CB potential of g-C3N4 (\(-1.13 \) eV vs NHE) is more negative than \( E_g (\text{O}_2^-/\text{O}_2^- = -0.046 \) eV vs NHE). Thus, g-C3N4 shows obvious transformation percentage of NBT (Fig. 9a), while that for pure BiVO4 (Fig. 9b) can be neglected. It can be concluded that there are almost no \( \text{O}_2^- \) produced from the electrons of BiVO4, because its CB potential (0.43 eV vs NHE) is more positive than \( E_g (\text{O}_2^-/\text{O}_2^- = -0.046 \) eV vs NHE), and the standard redox potential of Bi\(^{4+}/\text{Bi}^{3+} \) (1.59 eV) is more negative than that of \( \text{OH}/\text{OH}^- \) (+1.99 eV). For pure g-C3N4, the CB potential of g-C3N4 and BiVO4, most of electrons in the CB of BiVO4 were transferred to the VB of g-C3N4 and recombined with the holes there according to the above energy potentials analysis (Fig. 6), which enables the electrons remained in the CB of g-C3N4 to react with \( \text{O}_2^- \) to generate \( \text{O}_2 \) radicals. It was proved by the highest transformation percentage of NBT of BiVO4/g-C3N4 as shown in Fig. 9c. Moreover, the NBT transformation percentage of the 3:7 BiVO4/g-C3N4 composite is also higher than that of the mechanically mixed sample (Fig. 9d). These results demonstrate that the photogenerated electrons on the CB of BiVO4 could easily transfer to the VB of g-C3N4, resulting in more effective charge separation and reducing the probability of recombination of electron-hole pairs in the BiVO4/g-C3N4 composites. Especially, the 3:7 BiVO4/g-C3N4 holds more g-C3N4, leading to that more photogenerated electrons can react with \( \text{O}_2^- \) and take part in decomposition of RhB, which is in good agreement with the active species trapping experiments (Fig 5d).

Furthermore, the terephthalic acid photoluminescence probing technique (TA-PL) was also applied to investigate the \( \text{OH} \) radicals since TA could react with \( \text{OH} \) radicals to form a highly fluorescent 2-hydroxyterephthalic acid (TAOH). For pure BiVO4, there is almost no \( \text{OH} \) species generated because of the rapid decay through recombination of photoexcited charge carries. Compared with pure g-C3N4 (Fig. 10a) and BiVO4 (Fig. 10b), the highest PL intensity was observed over the 3:7 BiVO4/g-C3N4 composite as shown in Fig. 10c. This should be attributed to the Z-scheme charge transfer, which results in the enrichment of holes on the VB of BiVO4 to produce more...
between gXC photocatalytic performance than the individuals under visible-light irradiation. The detailed active species trapping and quantification experiments of \( \bullet O_2 \) and \( \bullet OH \) production over BiVO\(_4\)/g-C\(_{3}N_4\) composites and the individuals revealed that the significantly improved photocatalytic activity should be attributed to the fabrication of Z-scheme principled BiVO\(_4\)/g-C\(_{3}N_4\), which can result in the more efficient separation and largely reduced recombination probability of photoexcited electron-hole pairs, thus enabling highly powerful oxidation and reduction capability.

It was also verified by the PL spectra and photoelectrochemical experiments.

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### Notes and references


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**Fig. 1** (a) XRD patterns and (b) FTIR spectra of g-C$_3$N$_4$, BiVO$_4$ and BiVO$_4$/g-C$_3$N$_4$ composites with molar ratios of 1:9, 2:8, 3:7, 4:6 and 5:5.
Fig. 2 TEM images of the as-obtained samples: (a) g-C₃N₄, (b) BiVO₄, (c) 3:7 BiVO₄/g-C₃N₄; HRTEM images of (d, e) 3:7 BiVO₄/g-C₃N₄.
Fig. 3 (a) Typical XPS survey spectra of 3:7 BiVO$_4$/g-C$_3$N$_4$. High resolution XPS spectra of (b) Bi 4f, (c) V 2p, (d) O 1s, (e) C 1s, and (f) N 1s of 3:7 BiVO$_4$/g-C$_3$N$_4$. 
Fig. 4 UV-vis diffuse reflectance spectra of g-C_3N_4, BiVO_4, BiVO_4/g-C_3N_4 composites with molar ratios of 1:9, 2:8, 3:7, 4:6 and 5:5.
Fig. 5 (a) Photocatalytic degradation curves of RhB over as-prepared BiVO₄/g-C₃N₄ samples under the visible light irradiation (λ > 420 nm); (b) UV-visible spectra of RhB at different visible-irradiation-times in the presence of 3:7 BiVO₄/g-C₃N₄; (c) Apparent rate constants for the photodegradation of RhB over BiVO₄/g-C₃N₄ under visible light irradiation (λ > 420 nm); (d) Photocatalytic degradation of RhB over 3:7 BiVO₄/g-C₃N₄ photocatalysts alone and with the addition of TBA, EDTA, or BQ.
Fig. 6 Crystal structure of (a) BiVO₄ and (b) g-C₃N₄; (c) Schematic diagrams for interfacial charge transfer of BiVO₄/g-C₃N₄ Z-scheme photocatalyst.
Fig. 7 Photoluminescence spectra of g-C₃N₄, BiVO₄, and 3:7 BiVO₄/g-C₃N₄ photocatalysts.
Fig. 8 (a) Comparison of transient photocurrent responses of the g-C$_3$N$_4$, BiVO$_4$ and 3:7 BiVO$_4$/g-C$_3$N$_4$ and (b) EIS Nynquist plots of the g-C$_3$N$_4$ and 3:7 BiVO$_4$/g-C$_3$N$_4$ with light on/off cycles under visible light irradiation ($\lambda > 420$ nm, $[\text{Na}_2\text{SO}_4] = 0.1$ M).
Fig. 9 Spectra of NBT transformation generated by (a) 50mg of g-C₃N₄, (b) 50mg of BiVO₄, (c) 50mg of 3:7 BiVO₄/g-C₃N₄ and (d) mechanically mixed 35mg g-C₃N₄ with 15mg BiVO₄ under irradiation with visible light (λ > 420 nm).
Fig. 10 Fluorescence spectra of a TAOH solution generated by (a) 50mg of g-C₃N₄, (b) 50mg of BiVO₄, (c) 50mg of 3:7 BiVO₄/g-C₃N₄ and (d) mechanically mixed 35mg g-C₃N₄ with 15mg BiVO₄ under irradiation with visible light (λ > 420 nm)
Mediator-free direct Z-scheme photocatalytic system: BiVO$_4$/g-C$_3$N$_4$ organic-inorganic hybrid photocatalyst with highly efficient visible-light-induced photocatalytic activity

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Mediator-free Z-scheme BiVO$_4$/g-C$_3$N$_4$ photocatalysts were successfully obtained based on band gap engineering design. It exhibits high visible-light-driven photocatalytic activity for degradation of RhB and photocurrent generation. The much more powerful oxidation and reduction capability of the samples were demonstrated by the active species experiments, NBT transformation and TA-PL probing technique.