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Enhanced Interfacial Electronic Transfer of BiVO₄ Coupled with 2D g-C₃N₄ for Visible-light Photocatalytic Performance

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Abstract

A BiVO₄/2D g-C₃N₄ direct dual semiconductor photocatalytic system has been fabricated via electrostatic self-assembly method of BiVO₄ microparticle and g-C₃N₄ nanosheet. According to experimental measurements and first-principle calculations, the formation of built-in electric field and the opposite band bending around the interface region in BiVO₄/2D g-C₃N₄ as well as the intimate contact between BiVO₄ and 2D g-C₃N₄ will lead to high separation efficiency of charge carriers. More

importantly, the intensity of built-in electric field is greatly enhanced due to the ultrathin nanosheet structure of 2D g-C₃N₄. As a result, BiVO₄/2D g-C₃N₄ exhibits excellent photocatalytic performance with the 93.0% Rhodamine B (RhB) removal after 40 min visible light irradiation, and the photocatalytic reaction rate is about 22.7 and 10.3 times as high as that of BiVO₄ and 2D g-C₃N₄, respectively. In addition, BiVO₄/2D g-C₃N₄ also displays enhanced photocatalytic performance in the degradation of tetracycline (TC). It is expected that this work may provide insights into the understanding the significant role of built-in electric field in heterostructure and fabricating highly efficient direct dual semiconductor systems.

Keywords: BiVO₄; g-C₃N₄ nanosheet; photocatalytic degradation; built-in electric field; interfacial electronic effects

1. Introduction

The photocatalytic technology has been regarded as an effective and eco-friendly pathway to solve environmental issue by effectively utilizing solar energy[1,2]. However, the performance of single-phase semiconductor photocatalyst is greatly limited by its insufficient visible light response and easy recombination of carriers[3]. In order to solve these problems, considerable efforts have been devoted to construct a promising photocatalyst to improve the photocatalytic performance. Among different strategies, direct dual semiconductor systems construction has been considered a noteworthy strategy due to the combination of the reduced recombination of photogenerated electron-holes and the strong redox ability, which is more favorable

for the photocatalytic reactions[4]. In the direct dual semiconductor photocatalytic systems, the interfacial electronic transfer between different semiconductors has always been a difficult technical problem[5]. Therefore, more attention should be paid on how to construct an effective direct dual semiconductor system with high photocatalytic performance and the interfacial electronic effects are also worthy to be investigated in detail.

Some new visible light harvesting Bi-based photocatalysts, such as BiVO₄[6], BiWO₆[7], Bi₂O₂CO₃[8], Bi₂S₃[9], and BiOX (X=Cl, Br, I)[10,11], have drawn increasing attention due to the unique physical properties[12]. Among them, the monoclinic bismuth vanadate (m-BiVO₄) with the appropriate band gap of about 2.4 eV and negative valence band edge potential (about 2.5 eV vs. NHE) has been admitted as one outstanding photocatalyst[6]. However, the low conduction band minimum, poor charge transport performance and short life-time of photogenerated electron-holes are the obstacles to achieve a satisfactory photocatalytic efficiency for BiVO₄[13]. Thus, a full exploitation of BiVO₄ with strong oxidation ability highly necessitates the construction of direct dual semiconductor systems.

Alternatively, the metal-free graphite-like carbon nitride (g-C₃N₄) semiconductor with a moderate band gap of 2.7 eV and high photoelectrochemical and thermal stability has been proved to be an encouraging candidate material to couple with BiVO₄[14-16]. It is found that g-C₃N₄ possesses a relatively negative conduction band (CB) position (about -1.1 eV vs. NHE), which causes an excellent reduction ability of electrons on the CB of g-C₃N₄[17]. More attractively, the more negative CB edge

potential of g-C₃N₄ can match well with the energy levels of BiVO₄ to construct dual semiconductor systems[18]. For this reason, various dual semiconductor systems have been constructed, such as Ag@PCNS/BiVO₄[19], Ag@g-C₃N₄@BiVO₄[20], and so on. Although a breakthrough on above heterostructure is achieved, the present dual semiconductor systems typically have noble metals, leading to the relative high cost and low stability of these photocatalysts. Furthermore, there are still far from satisfaction about the enhancement of visible light photocatalytic performance. Firstly, bulk g-C₃N₄ with a large number of grain boundaries formed under high-temperature conditions can enhance the recombination rate of the charge carriers and then decrease the photocatalytic efficiency[21,22]. Secondly, g-C₃N₄ plays role in bulk g-C₃N₄ based architecture[23]. Therefore, it's necessary to adjust the structure of bulk g-C₃N₄ which is usually acted as photogenerated electrons donor in the BiVO₄/g-C₃N₄ dual semiconductor systems. It's revealed that two-dimensional (2D) g-C₃N₄ ultrathin nanosheet prepared by exfoliation from bulk g-C₃N₄ present a shift of CB edge to a more negative position which can be attributed to the quantum confinement effect derived from the decrease of particle size and layer numbers[24,25]. In addition, the 2D ultrathin nanosheet structure helps to shorten the transfer distance of interfacial charge and thus greatly boost the charge transportation from bulk to surface[26]. Up to now, seldom research is focused on addressing those issues in BiVO₄/g-C₃N₄ photocatalysts. Meanwhile, the interfacial electronic effects of the BiVO₄/2D g-C₃N₄ are also worthy to be investigated. Inspired by the above consideration, it is worth developing an efficient method to combine 2D g-C₃N₄ with BiVO₄ and further to

explore the interfacial charge carrier's transfer.

In this work, a BiVO₄/2D g-C₃N₄ direct dual semiconductor system with tight interfacial contact has been fabricated via a electrostatic self-assembly method. The synergistic interaction of the individual component of BiVO₄/2D g-C₃N₄ grants itself with effective light harvesting, large specific surface area and promoted capability of charge carriers separation. As a result, it's anticipated to exhibit extremely high photocatalytic performance for RhB degradation under visible light irradiation. What's more, the synergistic interaction between BiVO₄ and 2D g-C₃N₄ interface, and the structure-performance relationship over the BiVO₄/2D g-C₃N₄ has been investigated deeply by experiments and first-principles calculations. At the same time, the detailed mechanism is also further proposed and confirmed.

2.Experimental Section

2.1 Materials synthesis

BiVO₄ is prepared through a hydrothermal process. Firstly, Bi(NO₃)₃·5H₂O (1.21275 g) is dissolved in 20 mL HNO₃ solution (2 mol/L) with continuous stirring for 30 min, marked as solution A for Bi source. NH₄VO₃ (0.2925 g) is put into 20 mL NaOH solution (2 mol/L) and stirred for 30 min, marked as solution B for V source. Subsequently, Solution B is added slowly into solution A and stirred for another 1 h. After NaOH solution is added into the mixed solution to adjust the pH value to 7, the mixed solution is transferred into a 100 mL Teflon-lined autoclave and maintained at 180°C for 12 h, and then cooled down naturally. Finally, the yellow solid is

thoroughly washed and dried at 80°C for 12 h to get the BiVO₄.

2D g-C₃N₄ is prepared via a optimized thermal oxidation process. Firstly, the crucible containing melamine is put into muffle furnace and heated at 550°C for 4h in air to obtain bulk g-C₃N₄. Subsequently, the bulk g-C₃N₄ powder is putted into the crucible and heated at 550°C for 2 h in air. After cooling to room temperature, the obtained product further heated at 550°C for 2 h in air. Finally, a white powder of 2D g-C₃N₄ is obtained with a yield of about 5%.

The BiVO₄/2D g-C₃N₄ is constructed by electrostatic self-assembly method. Firstly, the as-prepared 2D g-C₃N₄ is added into 100 mL methanol and then placed in an ultrasonic bath for 1 h to obtain the homogeneous 2D g-C₃N₄ dispersion solution. The BiVO₄ powder is added into the homogeneous 2D g-C₃N₄ dispersion solution and continued sonicating for another 1 h and stirred in a fume hood for 24 h. After volatilization of the methanol, the resulting product is collected and dried at 60°C for 12h to obtain BiVO₄/2D g-C₃N₄ photocatalysts. The process is shown in Scheme 1.

2.2 Characterization of the photocatalysts

The Zeta potential is detected by a Zetasizer Nano S90 (Malvern Instruments, U.K.). In brief, the sample is dispersed in methanol by sonication. The crystal structure is analyzed by powder X-ray diffraction (XRD, D/MAX-2500 diffractometer, Rigaku, Japan) in the range of 10–70° at a scanning rate of 4° min⁻¹. The morphology and microstructures are observed on a field emission scanning electron microscopy (FE-SEM, S4800, Hitachi) and transmission electron microscope (TEM) (JEOL, JEM-2100F, Japan). The morphology and thickness of 2D g-C₃N₄ nanosheets are

studied on a Bruker Multimode 8 atomic force microscopy (AFM). The chemical compositions and electronic states are investigated by X-ray photoelectron spectroscopy (XPS) (ESCALab250Xi, Al K α). The UV–vis diffuse reflectance spectra (DRS) are obtained by a UV–vis-NIR spectrophotometer (Agilent Cary 5000) in the wavelength range of 200–800 nm and BaSO₄ is used as the reference. The Brunauere-Emmette-Teller (BET) specific surface area is measured by N₂ adsorption-desorption isotherms determined at 77 K on a Micromeritics ASAP 2020. Photoluminescence (PL) spectra are obtained on a F-7000 (Hitachi, Japan) luminescence spectrometer with an excitation wavelength at 365 nm. Total organic carbon (TOC) are monitored on a Vario TOC cube (Elementar). The electron spin resonance (ESR) are conducted with a ER200-SRC-10/12 spectrometer to detect the existence of defects as well as the formation of superoxide and hydroxide radicals in the photocatalytic processes with 5,5-dimethyl-1-pyrroline-Noxide (DMPO: 50 mM, 0.2 mL) as spin-trapped reagent. The intermediates generated are detected by liquid chromatography-tandem mass spectrometry (LC-MS) equipped with Q Exactive Orbitrap and Thermo Scientific Ultimate 3000 RSLC high resolution liquid chromatography.

2.3 Photoelectrochemistry measurement

The transient photocurrent response measurements are executed on an electrochemical work station (Shanghai Chenhua CHI-650E). The measurement is conducted in a conventional three-electrode system, a platinum wire as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode. 0.1M aqueous

Na₂SO₄ solution as electrolyte. For the measurements, a 500 W Xe lamp is used as light source with a bias of 0.5 V. The electrochemical impedance spectroscopy (EIS) is measured on a frequency range from 0.05 Hz–100 kHz with the current amplitude of 10 mV. The Mott-Schottky tests are obtained at the frequency of 1 KHz.

2.4 Photocatalytic performance tests

Photocatalytic degradation of RhB is carried out for evaluation of catalytic performance, which is conducted in an XPA-7 photochemical reactor (Xujiang Machine Factory, Nanjing, China). A 500 W Xe lamp is used as the light source with a cut-off filter ($\lambda \geq 420$ nm). The light source is positioned 10 cm over the surface of the suspension, and the light intensity is determined to be 300 mW/cm⁻². In each experiment, 10 mg sample is added into 50 mL RhB solution (10 mg L⁻¹) or 50 mL TC solution (10 mg L⁻¹). Before irradiation, the suspensions are stirred for 30 min in the dark to ensure adsorption-desorption equilibrium. At certain interval, 4 mL the suspensions are withdrawn from the photoreactor and centrifuged (5000 rpm/min) for 10 min to remove the photocatalysts. The concentration of the RhB and TC during the photoreaction is analyzed with a UV–vis spectrophotometer in a scanning range of 200~700 nm. Several consecutive reaction rounds are measured to determine the stability of the photocatalysts. Furthermore, a pseudo-first-order model ($\ln(C/C_0)=kt$, where C and C₀ are concentration of RhB solution at reaction time t and initial value, respectively, and k is the apparent rate constant.) to describe the photocatalytic kinetics.

2.5 Calculation method and model

Density functional theory (DFT) are performed using the Vienna ab initio simulation package (VASP) code[27,28]. The projector augmented wave (PAW) pseudopotential are employed to describe the electron-ion interaction[29]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) is adopted for the exchange and correlation potential[30,31]. To obtain more accurate electronic properties, the hybrid Heyd–Scuseria–Ernzerhof functional (HSE06) is used to correct the PBE band gaps[32]. The plane-wave cutoff energy of 500 eV and the Monkhorst–Pack grids in Brillouin Zone (BZ) of the reciprocal space is sampled as $0.01 \times 2\pi \text{ \AA}^{-1}$ has been used in this work. All the atoms in the unit cell are fully relaxed until the force on each atom is less than 0.01 eV/\AA , and the energy tolerances less than $1.0 \times 10^{-6} \text{ eV}$ per atom. Moreover, a vacuum region of 15 \AA is applied along the z direction. And the van der Waals (VDW) interactions are considered by adopting DFT-D3(BJ) with the Becke and Johnson (BJ)-damped method[33].

The optimized lattice parameters of BiVO_4 structure are $a = 7.337 \text{ \AA}$, $b = 11.748 \text{ \AA}$, $c = 5.177 \text{ \AA}$, and $\beta = 134.871^\circ$, respectively, which are consistent with in good agreement with the experimental values[34]. And our calculated parameter of the monolayer $g\text{-C}_3\text{N}_4$ ($a=7.140 \text{ \AA}$) is in good agreement with other simulated (7.140 \AA) and experimental results (6.810 \AA)[35,36]. In this work, BiVO_4 (010) surface, which is a more stable surface than the other low index surfaces of BiVO_4 , is chosen as the substrate. To make the lattice matched highly between BiVO_4 (010) surface and monolayer $g\text{-C}_3\text{N}_4$, a supercell structure (having 132 atoms) are built which include

132 atoms and a $\sqrt{17} \times \sqrt{2}$ unit cell of BiVO₄ (010) (Fig. S1a) and a 3×1 unit cell of g-C₃N₄ (001) (Fig. S1b), and the energetically favorable configurations is shown in Fig. S1c.

3. Results and discussion

3.1. Crystal structure and morphology properties

XRD patterns of the as-synthesized BiVO₄, 2D g-C₃N₄ and BiVO₄/2D g-C₃N₄ photocatalysts are presented in Fig. 1. The narrow and sharp diffraction peaks of BiVO₄ suggest a high crystallinity of monoclinic phase (JCPDS, No.14-0688). In the case of 2D g-C₃N₄, two diffraction peaks at 27.46° and 21.60° are indexed as the (002) and (100) crystal planes of g-C₃N₄ (JCPDS, No.87-1526), respectively, which is characteristic of interlayer stacking of conjugated aromatic system and in-plane repeated motif of the tri-s-triazine rings[36,37]. Especially, as shown in Fig. S2, compared with bulk g-C₃N₄, the intensity of (002) peak of 2D g-C₃N₄ significantly decreases, indicating that the 2D ultrathin nanosheet have been successfully exfoliated from bulk g-C₃N₄ as expected[38]. In comparison with BiVO₄ and 2D g-C₃N₄, it can be observed that 2D g-C₃N₄ and BiVO₄ co-exist in the BiVO₄/2D g-C₃N₄ photocatalysts, and no other impurities are formed in the preparation process.

The formation of 2D g-C₃N₄ is further verified by AFM image and the corresponding height profile. As shown in Fig. 1b and c, the average thickness of 2D g-C₃N₄ is around 2.0 nm. The theoretical thickness of monolayer g-C₃N₄ is 0.36 nm[39], and thus the 2D g-C₃N₄ is composed of five C–N layers, which indicates that the as-synthesized g-C₃N₄ possesses the 2D ultrathin nanosheet structure.

The morphology and structure information of the as-synthesized photocatalysts are investigated by SEM and TEM. It can be observed that BiVO₄ is composed of numerous of polyhedral irregular particles with smooth surface and size of about 2–3 μm (Fig. 2a). 2D g-C₃N₄ displays several stacking layers structure with a rippled and crumpled surface (Fig. 2b). In the BiVO₄/2D g-C₃N₄ photocatalysts (Fig. 2c), quantities of 2D g-C₃N₄ nanosheets are clustered on or anchored on BiVO₄ particles. In the TEM images, the as-synthesized BiVO₄ (Fig. 2d) possesses a plate-like morphology, which is in good agreement with the SEM results. The selected area electron diffraction (SAED) patterns show the single crystal nature of the BiVO₄ with good crystallinity (inset of Fig. 2d), the lattice space of 0.269 nm, 0.188 nm and 0.257 nm can be indexed to the (200), (-202) and (002) plane of monoclinic BiVO₄, respectively. The layered 2D g-C₃N₄ possesses large and 2D ultrathin nanosheets structure (Fig. 2e). Correspondingly, polycrystalline rings are obtained by the SAED technique (inset of Fig. 2e). From the TEM image of BiVO₄/2D g-C₃N₄ (Fig. 2f and Fig. 2g), it can be clearly seen that the firm connection between BiVO₄ and 2D g-C₃N₄ is achieved through a well-defined boundary. To estimate the formation process of BiVO₄/2D g-C₃N₄, the surface charge of BiVO₄, bulk g-C₃N₄ and 2D g-C₃N₄ are investigated. As shown in Fig. S3, the Zeta potential of bulk g-C₃N₄ and 2D g-C₃N₄ is -5.9 mV and 6.9 mV, respectively, which indicates that the surface charge of g-C₃N₄ will be changed from negative to positive with the treatment of thermal oxidation. Meanwhile, the Zeta potential of BiVO₄ is -7.1 mV. Thus, self-assembly formation of BiVO₄/2D g-C₃N₄ is achieved by electrostatic adsorption

between the negatively charged BiVO_4 and the positively charged 2D $\text{g-C}_3\text{N}_4$.

In order to further ascertain the phase distribution in the $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$ photocatalysts, HR-TEM image can be performed (Fig. 2h). It is apparent that the interplanar spacing about 0.309 nm is in agreement with the (121) lattice plane of BiVO_4 . In comparison, the anchored $\text{g-C}_3\text{N}_4$ on the BiVO_4 shows weak crystallinity with blurry lattices, which is the typical characteristic of $\text{g-C}_3\text{N}_4$ [16]. In addition, the SAED pattern measured at the $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$ (Fig. 2i) shows the combination of both BiVO_4 and 2D $\text{g-C}_3\text{N}_4$. Therefore, 2D $\text{g-C}_3\text{N}_4$ has been successfully tightly anchored on BiVO_4 . Theoretically, this formed intimate interface can be serves as photogenerated charge carriers channels will benefit for the charge transfer[3].

3.2. Interfacial interactions of $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$

To obtain insight into the interfacial electronic structures, the chemical compositions and electronic states of as-synthesized photocatalysts are investigated by XPS. In the survey spectrum (Fig. 3a), Bi, V, O, C and N elements are all detected in $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$ photocatalysts, which is accordance with the XRD results. In addition, for Bi 4f (Fig. 3b) and V 2p (Fig. 3c) spectra of BiVO_4 , two typical peaks at 158.80 eV and 164.10 eV are attributed to Bi 4f_{7/2} and Bi 4f_{5/2} induced by Bi^{3+} species, respectively[40,41], and two peaks of V 2p at 516.40 eV and 523.80 eV are respectively correspond to V 2p_{3/2} and V 2p_{1/2}. For C 1s (Fig. 3d) spectra of 2D $\text{g-C}_3\text{N}_4$, the peak at 284.55 eV is associated with the adventitious carbon[42], whereas the other C 1s peaks at 286.15 eV and 287.95 eV are indicative of sp^3 hybridized carbon in C-(N)_3 and sp^2 -hybridized carbon in N-C=N , respectively[43]. The N 1s

spectra of 2D g-C₃N₄ (Fig. 3e) divided into three peaks: one at 398.50 eV is due to C=N-C bonds, and the other two peaks at about 400.40 eV and 404.30 eV are attributed to characteristic chemical atoms group of N-(C)₃ and -NH₂, respectively[44]. For the O 1s spectra of BiVO₄ (Fig. 3f), the peak at 529.50 eV is attributed to the V-O of BiVO₄, and there is a weak shoulder at 530.55 eV which is related to hydroxylated oxygen or chemisorbed water molecule on the surface. After coupling 2D g-C₃N₄ with BiVO₄, two new independent peaks occur, one of which at 532.10 eV is related to the oxygen atoms in 2D g-C₃N₄, due to the absorbed water[25]. This is consistent with the O 1s found in the XPS survey spectrum (Fig. S4) of 2D g-C₃N₄ at 532.20 eV. In contrast, the peak corresponding to C-OH becomes much stronger for the BiVO₄/2D g-C₃N₄ (532.10 eV), suggesting that more C-OH groups are generated[45,46]. The increase in concentration of surface C-OH can further improve the surface hydrophilicity of the BiVO₄/2D g-C₃N₄, which is in favor of the generation of free radicals in the following photocatalytic oxidation process[47]. Therefore, compared with that of BiVO₄ and 2D g-C₃N₄ nanosheets, all the peaks of Bi 4f, V 2p, sp²-hybridized C1s in N-C=N, and N 1s spectra shifts to lower binding energy in BiVO₄/2D g-C₃N₄ photocatalysts, which means the change in electron density and is considered to be the evidence of the formation of heterojunction[48]. The XPS analysis further confirms the above XRD and TEM results and clearly proves the existence of heterojunction rather than a simple physical mixture.

It has been reported that the variation of binding energy is closely related to the change of surface electron density, which results from the directed charge transfer

between semiconductors with different Fermi levels[49]. The electron will transfer from one semiconductor with a higher Fermi level to another one with a lower Fermi level. DFT calculations are used to calculate the work function (Φ) according to the following equation: $\Phi = E_{\text{vac}} - E_{\text{F}}$, where E_{vac} and E_{F} are the electrostatic potential of the vacuum level and Fermi level, respectively. According to our calculations (Fig. S5), the electron will transfer from 2D g-C₃N₄ to BiVO₄ between heterojunction interface. Correspondingly, this charge transfer will lead to a decrease of electron concentration in 2D g-C₃N₄ and an increase in BiVO₄, thus, the binding energies of Bi 4f and V 2p decreased. However, the binding energies of C 1s and N 1s shift towards lower binding energies as revealed by XPS results, which is ascribed to the fact that more defect sites lead to a much higher concentration of delocalized electrons[50]. Further, the electron spin resonance (ESR) measurement can provide fingerprint evidences for structural defects. As shown in Fig. 4, both 2D g-C₃N₄ and BiVO₄/2D g-C₃N₄ exhibit a asymmetric signal centering at $g = 2.0034$, which can be ascribed to the unpaired electrons on the carbon atoms of the aromatic rings within π -bonded nanosized clusters[51]. The BiVO₄/2D g-C₃N₄ shows intensified ESR signal relative to that of 2D g-C₃N₄, revealing the much higher concentration of delocalized electrons in BiVO₄/2D g-C₃N₄ photocatalysts.

On the basis of the above results, Fig. S6 illustrates the interfacial charge transfer between BiVO₄ and 2D g-C₃N₄. As mentioned above, the work functions of BiVO₄(010) and g-C₃N₄ are 6.686 eV and 4.396 eV, respectively. When they touch each other in the heterojunction, the electrons in g-C₃N₄ will flow to BiVO₄(010)

across their interface until an equilibrium state is formed. Benefiting from the free electron redistribution, the surface of BiVO₄ is negatively charged and the surface of 2D g-C₃N₄ is positively charged. Naturally, a built-in electric field from 2D g-C₃N₄ (+) to BiVO₄ (-) is established at the contact interface, which causes the depletion or accumulation of free charge carrier around the semiconductor interface region. Simultaneously, the band edge of BiVO₄ bends downward, and that of 2D g-C₃N₄ bends upward. Specifically, in this work, the electrostatic energy experienced by the electrons moving through the interface can be envisioned as the direction of the bend. When the electrons in 2D g-C₃N₄ experiences repulsion from the negatively charged layer located in the BiVO₄, their potential energy rises and the bands bend upward, and vice versa[52]. As a result, the upward band bending allows holes to flow out freely while inhibits the electrons to flow out. On the contrary, electrons can move along the downward band bending but holes do not[52]. Under light excitation, the existence of the built-in electric field induces the recombination between photogenerated electrons in the CB of BiVO₄ and photogenerated holes in the VB of 2D g-C₃N₄ at the interface, which benefits the transfer of dual semiconductor systems photogenerated charge[53]. Therefore, it is expected that the built-in electric field and the opposite band bending are beneficial to the separation and transfer of charge. More importantly, due to the ultrathin nanosheets structure of 2D g-C₃N₄, the intensity of built-in electric field is greatly enhanced[3].

To accurately describe and confirm the interfacial electronic interaction of the heterojunction, the variation of electronic density of BiVO₄(010)/g-C₃N₄ is calculated

The discrepancy of interactions in BiVO₄(010)/g-C₃N₄ can be visualized by three-dimensional charge density difference of $\Delta\rho = \rho(\text{BiVO}_4(010)/\text{g-C}_3\text{N}_4) - \rho(\text{g-C}_3\text{N}_4) - \rho(\text{BiVO}_4(010))$, where $\rho(\text{BiVO}_4(010)/\text{g-C}_3\text{N}_4)$, $\rho(\text{g-C}_3\text{N}_4)$ and $\rho(\text{BiVO}_4(010))$ are the charge densities of the BiVO₄(010)/g-C₃N₄, g-C₃N₄ and BiVO₄(010), respectively. In Fig. 5a, the charge redistribution substantially appears in interface of BiVO₄(010) and g-C₃N₄. It can be obviously found that charge mainly accumulated around O and V atoms of BiVO₄, and the charge depletion is around g-C₃N₄, resulting in an build-in electric field. The build-in electric field actuated the photoelectrons to transfer from BiVO₄ to g-C₃N₄, then the photogenerated charge can be separated efficiently[54]. Fig. 5b exhibits the planar average charge density difference of BiVO₄(010)/g-C₃N₄ for several interlayer spacings along the Z-direction. The electron accumulation and depletion take place in BiVO₄(010) ($\Delta\rho > 0$) and g-C₃N₄ ($\Delta\rho < 0$) respectively, clearly demonstrated that the electrons transfer from g-C₃N₄ to BiVO₄(010). Based the above results, the build-in electric field of BiVO₄/2D g-C₃N₄ caused by interfacial electronic interaction, which is acted as a driving force for the transfer of the charge at the surface of semiconductors. The above calculations corroborate that the experimental and theoretical results are consistent well with each other.

3.3. Optical properties and specific surface area

The light absorption properties measured by UV-visible DRS of the as-synthesized photocatalysts have been illustrated in Fig. 7. The absorption edges of BiVO₄ and 2D g-C₃N₄ are approximately 532 nm and 458 nm, respectively, which

shows that both BiVO₄ and 2D g-C₃N₄ can work as visible light-excitabile photocatalysts. A combined absorption properties of the two compounds exhibit in BiVO₄/2D g-C₃N₄. The absorbance edge at about 475 nm is ascribed to 2D g-C₃N₄, while the absorption edge at about 584 nm shows slight red shift compared to BiVO₄[18]. The broader absorption in visible light region of BiVO₄/2D g-C₃N₄ may be ascribed to interfacial interaction between BiVO₄ and 2D g-C₃N₄[55]. Furthermore, the relative band gaps energy of BiVO₄ and 2D g-C₃N₄ can be calculated by the Tauc equation[56]: $\alpha h\nu = A(h\nu - E_g)^{n/2}$, where α , A, $h\nu$ and E_g represents absorption index, factor of proportionality, light energy and band gap energy, respectively. According to present reports, the value of n for BiVO₄ and 2D g-C₃N₄ are both 1[57,58]. Thus, as displayed in Fig. 7b, the band gap energy of BiVO₄ and 2D g-C₃N₄ are estimated to be 2.42 eV and 2.85 eV, respectively. The UV-vis DRS illustrated in Fig. S7 shows an obvious blue-shift for 2D g-C₃N₄ as compare to that of bulk g-C₃N₄, and the band gap energy bulk g-C₃N₄ is estimated to be 2.75 eV. The increased bandgap of 2D g-C₃N₄ can be attributed to the quantum confinement effect related to its decreasing layers[38].

The specific surface area and pore structure characteristics of as-synthesized photocatalysts are examined and shown in Fig. 8. The as-synthesized photocatalysts show the type IV isotherm with obvious H3 hysteresis loops, indicating the presence of mesoporous structures. The BET specific surface area (listed in the inset table) of the BiVO₄, 2D g-C₃N₄ and BiVO₄/2D g-C₃N₄ photocatalysts are 3.027, 101.601 and 87.521 m²/g, respectively. It can be seen that the incorporation of 2D g-C₃N₄ into the

layered structure of BiVO₄ can bring about a slight decrease of specific surface area. This result can be explained by the BiVO₄/2D g-C₃N₄ possess intimate interface interaction between BiVO₄ and 2D g-C₃N₄. Additionally, the corresponding relative pore volumes of three samples are 0.012, 0.498, 0.487 cm³/g, respectively. It indicates that BiVO₄/2D g-C₃N₄ with high specific surface area and the large pore volumes can provide abundant active sites for photocatalytic reaction.

3.4. Photocatalytic performance and stability

The photocatalytic performance of as-prepared samples are evaluated by photodegradation experiments of RhB under visible light irradiation ($\lambda \geq 420$ nm). Fig. 6a shows the UV-vis absorption spectra of RhB over BiVO₄/2D g-C₃N₄ at the photocatalytic degradation process. The absorption peak at 554 nm of RhB is significantly decreased with the increasing of irradiation time. The degradation efficiencies are shown in Fig. 6b. The blank test of RhB solution without photocatalysts shows little decrease under visible light irradiation, demonstrating that the self-photodegradation of RhB is almost negligible. The BiVO₄/2D g-C₃N₄ photocatalysts displays remarkably enhanced photocatalytic activity of 93.0% in 40 min under visible light irradiation, exceeding that of BiVO₄ (only 4.1%) and 2D g-C₃N₄ (13.0%) by a factor of 23 and 7, respectively. Meanwhile, the mechanically mixed BiVO₄/2D g-C₃N₄ photocatalysts has been prepared in this work with respect to the degradation of RhB under visible light irradiation. It is clearly observed that the photocatalytic performance of mechanically mixed sample is much lower than that of BiVO₄/2D g-C₃N₄, which indicates that the enhanced photocatalytic

performance of BiVO₄/2D g-C₃N₄ can be strongly attributed to the formed heterostructure between BiVO₄ and 2D g-C₃N₄. In addition, we tested TOC before and after photocatalytic degradation reaction of RhB to evaluate the mineralization efficiency[59]. TOC removal efficiency (Fig. S8) of BiVO₄/2D g-C₃N₄ is 52.7% after 120 min reaction, higher than that of BiVO₄ (25.1%) and 2D g-C₃N₄ (28.1%). That is, the prepared composites has strong capacity for RhB mineralization, indicating the synergistic interactions between BiVO₄ and 2D g-C₃N₄. Moreover, BiVO₄/2D g-C₃N₄ also displays enhanced photocatalytic performance in the degradation of TC (Fig. S9).

According to the equation ($\ln(C/C_0)=kt$ [60], (where C and C₀ are concentration of RhB solution at reaction time t and initial value, respectively, and k is the apparent rate constant.), the constant k of different photocatalysts are calculated and clearly showed in Fig. 6c. The apparent rate constant for the BiVO₄/2D g-C₃N₄ is 0.04276 min⁻¹, nearly 22.7 and 10.3 times as high as that of the BiVO₄ (0.00188 min⁻¹) and 2D g-C₃N₄ (0.00415 min⁻¹) and much higher than that of the mechanically mixed BiVO₄/2D g-C₃N₄ (0.01052 min⁻¹). The highest k value further confirms that the heterostructure formed between BiVO₄ and 2D g-C₃N₄ can enhance the photocatalytic performance.

In addition, the photochemical stability and recyclability of BiVO₄/2D g-C₃N₄ photocatalysts is investigated by the cycling experiments. As shown in Fig. 6d, the photocatalytic degradation efficiency of the BiVO₄/2D g-C₃N₄ show no significant change after four runs, illustrating the excellent repeatability. Furthermore, the XRD analysis of the BiVO₄/2D g-C₃N₄ after four cycles has been done (Fig. S10). Similar

to those of fresh sample, there is almost no difference in the XRD patterns of used samples. Therefore, the BiVO₄/2D g-C₃N₄ possess excellent stability during the photodegradation process.

3.5 Photophysical and photochemical properties

The separation efficiency of the charge carriers play a crucial role in photocatalytic reaction. Herein, the transient photocurrent response and EIS are performed to investigate the photogenerated charge carriers transfer and separation behaviors in photocatalysts. The transient photocurrent response with several on-and-off cycles of intermittent illumination of the photocatalysts have been carried out to reflect the quantities of electron-holes pairs during the photocatalytic reaction (Fig. 9a). Compared with BiVO₄ and 2D g-C₃N₄, BiVO₄/2D g-C₃N₄ shows a faster and more obvious photocurrent response when the light is on and a quicker decrease when the light is off. In addition, BiVO₄/2D g-C₃N₄ exhibits a significantly increased photocurrent intensity under visible light irradiation, 5.6 and 2.8 times of that of BiVO₄ and 2D g-C₃N₄, implying an enhanced efficiency in the separation of the charge carriers in BiVO₄/2D g-C₃N₄, which will provide a faster transfer of charge between BiVO₄ and 2D g-C₃N₄ and further improve the photocatalytic reaction. Meanwhile, EIS is also an effective method to reflect separation efficiency of the charge carriers. As shown in Fig. 9b, the smallest arc radius of BiVO₄/2D g-C₃N₄ indicates the smallest charge transfer resistance, the most effective electron-hole pair separation and the highest charge transfer, which is in agreement with the results of the photocurrent response. Moreover, the arc radius of samples under visible light

are smaller than in darkness, which can be attributed to the generation of charge. Thus, it can be reasonably concluded that the coupling of 2D g-C₃N₄ with BiVO₄ is beneficial for separation and transport kinetics of charge, resulting in the higher photocatalytic performance.

The PL spectroscopy is an important method to investigate the recombination degree of charge carriers. Generally, a lower PL intensity indicates a weaker recombination process of the charge carriers[61,62]. Fig. 9c presents the PL spectra of BiVO₄, 2D g-C₃N₄ and BiVO₄/2D g-C₃N₄ with an excitation wavelength of 365 nm. The corresponding signals of all the three photocatalysts can be listed as following: BiVO₄/2D g-C₃N₄ < BiVO₄ < 2D g-C₃N₄, which is in good accordance with the results of photocatalytic performance. Compared with BiVO₄ and 2D g-C₃N₄, BiVO₄/2D g-C₃N₄ exhibits the weakest PL peak intensity, which demonstrates that more charge in BiVO₄/2D g-C₃N₄ prefer to migrating onto the surface to participate the photocatalytic reaction. Additionally, to further confirm the enhancement of charge carriers separation efficiency of BiVO₄/2D g-C₃N₄, we also measure the time-resolved fluorescence spectra (Fig. 9d). The timedecay fluorescence curves can be fitted well to a double exponential function ($R(t) = B_1e_1^{-t/\tau_1} + B_2e_2^{-t/\tau_2}$), where B₁ and B₂ are the pre-exponential factor, and τ_1 and τ_2 are the radiative lifetime. Moreover, the average radiative lifetime (τ) is calculated through the following equation (Eq(1)):

$$\tau = \frac{B_1\tau_1^2 + B_2\tau_2^2}{B_1\tau_1 + B_2\tau_2} \quad (1)$$

The value of τ is 3.89, 3.75 and 4.52 ns for BiVO₄, 2D g-C₃N₄, and BiVO₄/2D

g-C₃N₄, respectively. That is to say, the increased τ of charge carriers for BiVO₄/2D g-C₃N₄ can enhance the probability of their involvement in the photocatalytic reaction before recombination[45,63], which is in accordance with the above results.

3.6 Photocatalytic mechanism

To obtain insight into enhanced photocatalytic mechanism of BiVO₄/2D g-C₃N₄, the total density of state (TDOS) and partial density of state (PDOS) are calculated by using DFT with HSE06 method (Fig. 10). The calculated electrical gap are 2.47 eV, 2.72 eV for BiVO₄(010) and g-C₃N₄, respectively, which are consistent with experimental values by UV-visible DRS. For BiVO₄(010) (Fig. 10a), the valence band maximum (VBM) is mainly comprised of O 2p states, and the conduction band minimum (CBM) is chiefly consisted of V 3d anti-bonding states, including some hybridization with O 2p states. For g-C₃N₄ (Fig. 10b), the VBM is mainly dominated by N 2p states, including some hybridization with the C 2p states, and the CBM is composed by strong hybridization between C 2p and N 2p electrons. Interestingly, for BiVO₄(010)/g-C₃N₄ (Fig. 10c), the VBM is majorly dominated by N 2p states of g-C₃N₄, while the CBM is occupied by the V 3d of BiVO₄(010). Thus, when the visible light irradiates BiVO₄(010)/g-C₃N₄, the electrons in the g-C₃N₄ N 2p states prefer to be directly excited into the V 3d states[64]. That is to say, the newly formed N 2p states in the VB possess a higher energy than that of O 2p states of BiVO₄, leading to an easier electronic transition from the VB to the CB in the BiVO₄(010)/g-C₃N₄. Therefore, the introduction of 2D g-C₃N₄ can improve the photocatalytic performance of BiVO₄ by increasing its visible light response, which is

also consistent with the UV-visible DRS result. Moreover, the incorporation of BiVO₄ cause the decline of hybrid electron density in the CB of 2D g-C₃N₄, which favors the electrons in CB to migrate easily to the surface of 2D g-C₃N₄. These results not only verify the experimental understanding of enhanced photocatalytic performance of the BiVO₄/2D g-C₃N₄, but also exhibit the microscopic charge migration process.

The CB positions of BiVO₄ and 2D g-C₃N₄ photocatalysts can be obtained by Mott-Schottky tests. As shown in Fig. S11, the positive slopes of Mott-Schottky plots of both BiVO₄ and 2D g-C₃N₄ indicate their nature of n-type semiconductor. Moreover, the flat-band potentials of BiVO₄ and 2D g-C₃N₄ are 0.28 eV and – 1.00 eV (vs Ag/AgCl), respectively. In general, the above flat band potential (E_{fb}) measured according to Ag/AgCl can be converted into the normal hydrogen electrode (NHE) potentials via the following equation: $E_{NHE} = E_{Ag/AgCl} + 0.6$ [65]. Furthermore, as the lowest potential of the CB of undoped n-type semiconductor is 0.3 eV more negative than E_{fb} [66], thus, the CB positions of BiVO₄ and 2D g-C₃N₄ are calculated to be 0.58 eV and – 0.70 eV (vs NHE), respectively. Combined with their band gaps, the corresponding VB positions of BiVO₄ and 2D g-C₃N₄ are 3.00 eV and 2.15 eV (vs. NHE), respectively.

The active species detected by the trapping experiment play a major role in explaining the photocatalytic mechanism. The 1,4-benzoquinone (BQ, 1mmol), ethylene diamine tetra-acetic acid disodium salt (EDTA-2Na, 1mmol), and isopropanol (IPA, 0.5ml) is added to the reaction system as the scavengers of superoxide radicals ($\cdot O_2^-$), holes (h^+) and hydroxyl radicals ($\cdot OH$), respectively. With

the addition of BQ, EDTA-2Na and IPA, the degradation efficiency decreases seriously from 93.0% to 14.0%, 83.6% and 48.0% , respectively (Fig. S12). It indicates that $\cdot\text{O}_2^-$ is the most important active species in the photocatalytic process, while $\cdot\text{OH}$ plays an auxiliary role in the degradation of RhB followed by h^+ .

In order to further investigate the radical generation in the photocatalytic system over the $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$, the ESR spin-trap technique with the DMPO is performed to trap $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals generated in the photocatalytic processes. As shown in Fig. S13, no ESR signal is observed at dark conditions for $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$. Six characteristic peaks of $\text{DMPO}\cdot\text{O}_2^-$ are detected in aqueous solution with the visible light on (Fig. S13a), suggesting that the photogenerated electrons in the CB of $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$ can be reacted with O_2 to generate $\cdot\text{O}_2^-$ radicals in the photodegradation process. Additionally, four characteristic peaks ESR signal of $\text{DMPO}\cdot\text{OH}$ with an intensity ratio of 1:2:2:1 have been detected under visible light irradiation (Fig. S13b), which means that $\cdot\text{OH}$ is also generated at the photocatalysts surface. Thus, the ESR analysis further confirms that the presence of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ in the photocatalytic process of $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$.

To understand the RhB degradation mechanism by $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$, the intermediate products are measured by LC-MS (Fig. S14). In light of m/z values, a possible pathway for RhB degradation is illustrated in Fig. S15. In the first step, N-ethyl is removed from RhB molecule ($m/z = 443.23$) by the active species, thereby producing N-de-ethylated intermediates ($m/z = 301.14$ and 415.20). Then, with reaction of photoliving groups with organics ($m/z = 173.08, 229.14, 279.16$ and

167.11), the bond between the amino group of the chromophore structure and the phenyl group may be broken[67]. Subsequently, the opening of the heterocyclic ring brings about small organic acid molecule($m/z = 116.99, 134.12$ and 149.01)[68]. And these intermediates will eventually be oxidized into CO_2 and H_2O .

It is generally acknowledged that the charge transfer mechanism in heterojunction has several types. Based on the band structures and edge positions of BiVO_4 and 2D $\text{g-C}_3\text{N}_4$, both the type-II heterojunction system and direct dual semiconductor system may be involved in the photocatalytic process of $\text{BiVO}_4/2\text{D g-C}_3\text{N}_4$ [69]. In type-II heterojunction system (Fig. 11a), the photogenerated electrons in the CB of 2D $\text{g-C}_3\text{N}_4$ will move to the CB of BiVO_4 , meanwhile, the holes in the VB have opposite migration direction. It is noteworthy that the CB potential of BiVO_4 is positive than the standard potential of $\text{O}_2/\cdot\text{O}_2^-$ (-0.33 eV vs. NHE). And the VB potential of 2D $\text{g-C}_3\text{N}_4$ is lower than the standard potential of $\cdot\text{OH}/\text{OH}^-$ (2.40 eV vs. NHE). Consequently, $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ species cannot be produced, which is in contradiction with the trapping experiments. Furthermore, it is difficult for the type-II charge transfer due to the built-in electric field at interface from 2D $\text{g-C}_3\text{N}_4$ to BiVO_4 and the certain degree of interface barrier.

On the basis of the above analysis, the dual semiconductor system is proposed and illustrated in Fig. 11b. Under visible light irradiation, the electrons are excited from VB of BiVO_4 and 2D $\text{g-C}_3\text{N}_4$ to their CB. Meanwhile, the holes are remained in the VB. Then, the built-in electric field and opposite band bending accelerate the recombination of some electrons (from CB of BiVO_4) and holes (from VB of 2D

g-C₃N₄) at the interface of them. Simultaneously, the holes retain in the VB of BiVO₄ and electrons retain in the CB of 2D g-C₃N₄ migrate to their surface, respectively. Whereafter, O₂ molecules dissolved in water combined with electrons of 2D g-C₃N₄ for generation of ·O₂⁻. While the holes in the VB of BiVO₄ oxidize the surface OH⁻ or H₂O for generation of ·OH. As a consequence, RhB is decomposed by ·O₂⁻ and ·OH reactive species. In the dual semiconductor system, all the charge transfer between BiVO₄ and 2D g-C₃N₄ can achieve efficient charge carriers separation and preserve their high reduction and oxidation ability simultaneously.

4. Conclusions

In summary, a BiVO₄/2D g-C₃N₄ direct dual semiconductor photocatalytic system with tight interfacial contact has been fabricated via electrostatic self-assembly method of BiVO₄ microparticle and g-C₃N₄ nanosheet. The strong electronic coupling in BiVO₄/2D g-C₃N₄ interface can induce charge transfer from 2D g-C₃N₄ to BiVO₄, leading to the formation of built-in electric field and the opposite bands bending around interface region. And more importantly, due to the ultrathin nanosheet structure of 2D g-C₃N₄, the intensity of built-in electric field is greatly enhanced. Under visible light irradiation, the intensive interfacial electronic effects as well as the dual semiconductor charge transfer mechanism can lead high separation efficiencies of photogenerated charge carriers and strong redox capability, and then more efficient photocatalytic degradation of RhB. This work highlights the effect of interfacial coupling between BiVO₄ and 2D g-C₃N₄ and verifies the significant of the built-in electric field in the heterojunction photocatalysts.

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Figure captions list

Scheme 1. Schematic illustration for the fabrication of BiVO₄/2D g-C₃N₄.

Fig. 1. XRD patterns of the prepared BiVO₄, 2D g-C₃N₄ and BiVO₄/2D g-C₃N₄, (b) AFM image of 2D g-C₃N₄ (c) the corresponding thickness analysis.

Fig. 2. SEM images of (a) BiVO₄, (b) 2D g-C₃N₄, (c) BiVO₄/2D g-C₃N₄, TEM image

of (d) BiVO₄, (e) 2D g-C₃N₄ (inset is SAED pattern), (f,g) BiVO₄/2D g-C₃N₄, HRTEM image of (h) BiVO₄/2D g-C₃N₄ and SAED pattern of (i) BiVO₄/2D g-C₃N₄.

Fig. 3. (a) XPS survey spectrum of BiVO₄, 2D g-C₃N₄, BiVO₄/2D g-C₃N₄, high resolution XPS spectra of (b) Bi 4f, (c) V 2p, (d) C 1s, (e) N1s and (f) O 1s obtained from BiVO₄, 2D g-C₃N₄, BiVO₄/2D g-C₃N₄.

Fig. 4. ESR spectra of BiVO₄, 2D g-C₃N₄ and BiVO₄/2D g-C₃N₄.

Fig. 5. (a) The sides view of charge density difference, and the yellow and cyan regions indicate electron accumulation and depletion, respectively. (b) The average electron density difference ($\Delta\rho$) along Z-direction for BiVO₄(010)/g-C₃N₄, where the positive value indicates electron accumulation, and the negative value indicates electron depletion.

Fig. 6. (a) UV–vis absorption spectral changes of RhB over the BiVO₄/2D g-C₃N₄. (b) The photocatalytic performance towards RhB degradation under visible light. (c) Kinetic fit for the degradation of RhB in the presence of different photocatalysts. (d) Cycling runs of BiVO₄/2D g-C₃N₄ for the degradation of RhB under visible light irradiation.

Fig. 7. (a) UV-visible DRS of BiVO₄, 2D g-C₃N₄ and BiVO₄/2D g-C₃N₄ (b) Band gap energy of BiVO₄ and 2D g-C₃N₄.

Fig. 8. Nitrogen adsorption-desorption isotherms and pore volume of BiVO₄, 2D g-C₃N₄ and BiVO₄/2D g-C₃N₄.

Fig. 9. (a) Transient photocurrent responses, (b) EIS Nyquist plots, (c) PL spectra, and (d) time-resolved fluorescence decay curves of BiVO₄, 2D g-C₃N₄, BiVO₄/2D

g-C₃N₄.

Fig. 10. The TDOS and corresponding PDOS of (a) BiVO₄ (010), (b) g-C₃N₄ and (c) BiVO₄(010)/g-C₃N₄. The Fermi level is represented the by the dotted line.

Fig. 11. Schematic illustration of photogenerated charge transfer for (a) type-II system and and (b) dual semiconductor system.