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2D/2D Black Phosphorus/g-C₃N₄ S-Scheme Heterojunction Photocatalysts for CO₂ Reduction Investigated using DFT Calculations

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Abstract: Photocatalytic reduction of CO₂ to hydrocarbon compounds is a promising method for addressing energy shortages and environmental pollution. Considerable efforts have been devoted to exploring valid strategies to enhance photocatalytic efficiency. Among various modification methods, the hybridization of different photocatalysts is effective for addressing the shortcomings of a single photocatalyst and enhancing its CO₂ reduction performance. In addition, metal-free materials such as g-C₃N₄ and black phosphorus (BP) are attractive because of their unique structures and electronic properties. Many experimental results have verified the superior photocatalytic activity of a BP/g-C₃N₄ composite. However, theoretical understanding of the intrinsic mechanism of the activity enhancement is still lacking. Herein, the geometric structures, optical absorption, electronic properties, and CO₂ reduction reaction processes of 2D/2D BP/g-C₃N₄ composite models are investigated using density functional theory calculations. The composite model consists of a monolayer of BP and a tri-s-triazine-based monolayer of g-C₃N₄. Based on the calculated work function, it is inferred that electrons transfer from g-C₃N₄ to BP owing to the higher Fermi level of g-C₃N₄ compared with that of BP. Furthermore, the charge density difference suggests the formation of a built-in electric field at the interface, which is conducive to the separation of photogenerated electron-hole pairs. The optical absorption coefficient demonstrates that the light absorption of the composite is significantly higher than that of its single-component counterpart. Integrated analysis of the band edge potential and interfacial electronic interaction indicates that the migration of photogenerated charge carriers in the BP/g-C₃N₄ hybrid follows the S-scheme photocatalytic mechanism. Under visible-light irradiation, the photogenerated electrons on BP recombine with the photogenerated holes on g-C₃N₄, leaving photogenerated electrons and holes in the conduction band of g-C₃N₄ and the valence band of BP, respectively. Compared with pristine g-C₃N₄, this S-scheme heterojunction allows efficient separation of photogenerated charge carriers while effectively preserving strong redox abilities. Additionally, the possible reaction path for CO₂ reduction on g-C₃N₄ and BP/g-C₃N₄ is discussed by computing the free energy of each step. It was found that CO₂ reduction on the composite occurs most readily on the g-C₃N₄ side. The reaction path on the composite is different from that on g-C₃N₄. The heterojunction reduces the maximum energy barrier for CO₂ reduction from 1.48 to 1.22 eV, following the optimal reaction path. Consequently, the BP/g-C₃N₄ heterojunction is theoretically proven to be an excellent CO₂ reduction photocatalyst. This work is helpful for understanding the effect of BP modification on the photocatalytic activity of g-C₃N₄. It also provides a theoretical basis for the design of other high-performance CO₂ reduction photocatalysts.

Key Words: Photocatalysis; CO₂ reduction; Step-scheme heterojunction; Graphitic carbon nitride; Density functional theory

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理论计算研究二维/二维 BP/g-C₃N₄ 异质结的光催化 CO₂ 还原性能费新刚¹, 谭海燕^{2,*}, 程蓓¹, 朱必成^{1,*}, 张留洋^{1,*}¹ 武汉理工大学, 材料复合新技术国家重点实验室, 武汉 430070² 湖北民族大学, 化学与环境工程学院, 湖北 恩施 445000

摘要: 光催化二氧化碳还原成烃类化合物是解决能源短缺和环境污染的重要途径。而构建复合物光催化剂可以有效地解决单一光催化剂的缺点, 并且提高二氧化碳还原活性。尽管对复合物光催化剂已经做了很多研究, 然而对其活性增强的内在机制还缺乏理论认识。本文采用密度泛函理论计算方法研究了二维/二维BP/g-C₃N₄复合模型的电子性质和CO₂还原反应过程。通过对能带位置和界面电子相互作用的综合分析发现, 在BP/g-C₃N₄异质结中, 光生载流子的迁移遵循S型异质结光催化机制。与单一的g-C₃N₄相比, 这种异质结可以实现光生载流子的高效分离并且拥有良好的氧化还原能力。此外, 通过对比研究CO₂在g-C₃N₄和BP/g-C₃N₄还原反应过程发现, 异质结使CO₂还原反应的最大能垒从1.48 eV降低到1.22 eV。因此, BP/g-C₃N₄异质结在理论上被证明是一种优良的CO₂还原光催化剂。这项工作有助于了解BP改性对g-C₃N₄光催化活性的影响, 也为其他高性能CO₂还原光催化剂的设计提供理论依据。

关键词: 光催化; CO₂还原; S型异质结; g-C₃N₄; 理论计算
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1 Introduction

Excessive CO₂ emission resulted from the combustion of fossil fuels leads to serious greenhouse effect and climate change¹⁻³. It is urgent to explore clean and effective methods to reduce CO₂ release. Under this circumstance, photocatalytic CO₂ reduction arouses wide attention, because it converts harmful CO₂ into valuable hydrocarbons^{4,5}. CO₂ is reduced assisted by photocatalysts and light irradiation⁶. Graphitic carbon nitride (g-C₃N₄) is a popular metal-free photocatalyst used for CO₂ reduction^{7,8}. It has several advantages such as nontoxicity, narrow bandgap and good physicochemical stability^{9,10}. Moreover, its considerably negative conduction band meets the thermodynamic requirement of CO₂ reduction to all kinds of products. However, the photocatalytic CO₂ reduction activity of pristine g-C₃N₄ is extremely poor¹¹.

Various strategies have been developed to enhance the photocatalytic activities of g-C₃N₄, among which the hybridization with others proves to be effective¹²⁻¹⁵. Enormous composites have been explored including CdMoO₄/g-C₃N₄¹⁶, BiVO₄/g-C₃N₄¹⁷, Bi₂MoO₆/g-C₃N₄¹⁸, Cd_xZn_yS/g-C₃N₄¹⁹, graphene/g-C₃N₄²⁰, and Ti₃C₂/g-C₃N₄²¹. Recently, black phosphorus (BP) has been employed to improve the photocatalytic performance of g-C₃N₄ in diverse areas^{22,23}. For example, Qiu *et al.* prepared BP decorated g-C₃N₄ nanosheet through a post calcination process²⁴. The optimal BP/g-C₃N₄ composite exhibited a high nitrogen fixation rate of 347.5 μmol·L⁻¹·h⁻¹, exceeding Pt deposited g-C₃N₄. Kong *et al.* synthesized BP quantum dot loaded g-C₃N₄ photocatalyst *via* a high-vacuum stirring method²⁵. With the BP percentage of 7%, the H₂ production rate was 3.6 times larger than that of unloaded g-C₃N₄. Wang *et al.* fabricated a BP/g-C₃N₄ nanohybrid composed of BP quantum dot and tubular g-C₃N₄²⁶. The novel

0D/1D structure showed excellent photocatalytic activity towards Cr (VI) reduction and oxytetracycline hydrochloride degradation.

Nevertheless, report on CO₂ reduction of BP/g-C₃N₄ photocatalyst is scarce. Han *et al.* prepared BP quantum dot modified g-C₃N₄ photocatalyst using an electrostatic attraction method and tested its CO₂ reduction activity²⁷. The CO production rate of BP/g-C₃N₄ was 2.5 times higher than that pristine g-C₃N₄. Although enhanced photocatalytic activities were achieved in the above examples, they merely speculated that promoted separation of photogenerated charge carriers were the intrinsic mechanism for the activity enhancement, while the essential function of BP modification was not explicitly investigated. There is still controversy over the role of BP. Some regarded it as a hole-migration cocatalyst whereas some deemed it as an electron mediator^{28,29}. Others also claimed that BP/g-C₃N₄ composite was a type-II heterojunction photocatalyst³⁰. Besides, no study has paid attention to the CO₂ reduction reaction process on BP/g-C₃N₄ composite.

Herein, to reveal the underlying mechanism of the improved CO₂ reduction performance of BP/g-C₃N₄ composite photocatalyst, theoretical study using density functional theory calculations is conducted. A 2D/2D BP/g-C₃N₄ composite model is built, and its photocatalytic behavior is meticulously evaluated. The geometric structure, electronic property, charge transfer, and CO₂ reduction reaction process of this model are systematically investigated. It is anticipated that this work can provide references for the interpretation of other g-C₃N₄-based or BP-modified photocatalysts.

2 Calculation methods

All the density functional theory calculations were carried out

by using the Vienna *ab initio* simulation package^{31,32}. The interaction between electrons and ion nucleus was implemented by the projector augmented wave (PAW) method³³. The exchange-correlation interactions were performed utilizing the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE)³⁴. DFT-D method of Grimme was employed to describe the van der Waals (vdW) interaction^{35,36}. A 450 eV cutoff energy was adopted to expand the electron wave functions. For Brillion zone, the Monkhorst-Pack grid with a $3 \times 3 \times 1$ k -point was used for geometry optimization and property calculation³⁷. A vacuum space of 1.5 nm was applied to eliminate interactions between neighboring images. In geometry optimization, all atoms were fully relaxed, and the convergence criteria for energy and force were set to 10^{-5} eV and $0.1 \text{ eV} \cdot \text{nm}^{-1}$, respectively. Due to the well-known underestimation of band gap (E_g) in the GGA-PBE functional, the Heyd-Scuseria-Ernzerhof 2006 (HSE06) hybrid functional was adopted to acquire precise energy gap values³⁸.

The change in Gibbs free energy (ΔG)^{39,40} is defined as:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{PH}} + \Delta G_{\text{U}} \quad (1)$$

where ΔE is the electronic energy difference, ΔE_{ZPE} and ΔS are the change in zero-point energy and entropy, respectively. T is the temperature (298.15 K). ΔG_{PH} is the correction of the H^+ free energy by the concentration, and it is equal to $k_{\text{B}} \times T \times \ln 10 \times \text{pH}$, where k_{B} is the Boltzmann constant and pH is set to be zero for acidic condition. ΔG_{U} is calculated by $-neU$, where n is the number of transferred electrons and U is the electrode potential. Zero-point energies are calculated from the vibrational frequencies through fixing the catalyst on the bottom (the vibrations of substrate were ignored). The entropies of isolated gas are obtained from the NIST database. The adsorption energy (E_{ads}) is computed by the formula:

$$E_{\text{ads}} = E_{\text{sub+a}} - E_{\text{sub}} - E_{\text{a}} \quad (2)$$

where $E_{\text{sub+a}}$, E_{sub} and E_{a} represent the total energies of substrate with adsorbed species, pure substrate without adsorbate, and

pure adsorbate, respectively.

3 Results and discussions

3.1 Geometric structures

The optimized cell parameters of g- C_3N_4 are $a = b = 0.71 \text{ nm}$, $\gamma = 120^\circ$, and those of BP are $a = 0.45 \text{ nm}$, $b = 0.33 \text{ nm}$, $\gamma = 90^\circ$. These parameters are consistent with the values in previous experimental and theoretical studies^{41,42}. 2D/2D BP/g- C_3N_4 heterojunction was built by placing monolayer g- C_3N_4 above the surface of monolayer BP. To realize a small lattice mismatch between the two components, a 2×2 monolayer g- C_3N_4 supercell composed of 24 C atoms and 32 N atoms was constructed (Fig. 1a), and its lattice constant was $a = b = 1.42 \text{ nm}$. Meanwhile, rhombic monolayer BP containing 48 P atoms was cleaved from 2×3 bulk BP with the diagonal as the surface edge (Fig. 1b), and its lattice constant was $a = b = 1.48 \text{ nm}$. Subsequently, an appropriate BP/g- C_3N_4 composite model was obtained by stacking the two layers.

The optimized structure of BP/g- C_3N_4 heterojunction is shown in Fig. 1c. The g- C_3N_4 layer in the composite presents a corrugated structure instead of the planar structure in pristine g- C_3N_4 , and the distortion degree ($h1$) is 0.15 nm . The upright height ($h2$) of BP layer in the composite is 0.26 nm , larger than that in pristine BP (0.21 nm). The equilibrium distance (d) between BP and g- C_3N_4 is 0.26 nm , in agreement with other g- C_3N_4 -based heterojunctions⁴³. The equilibrium distance conforms to the structural characteristics of vdW heterojunction, indicating that a vdW interaction is established between BP and g- C_3N_4 . To examine the stability of the BP/g- C_3N_4 composite structure, interface adhesion energy (E_{adh}) is evaluated by the following equation:

$$E_{\text{adh}} = E(\text{BP/g-}\text{C}_3\text{N}_4) - E(\text{g-}\text{C}_3\text{N}_4) - E(\text{BP}) \quad (3)$$

where $E(\text{BP/g-}\text{C}_3\text{N}_4)$, $E(\text{g-}\text{C}_3\text{N}_4)$ and $E(\text{BP})$ are the total energies of BP/g- C_3N_4 hybrid, monolayer g- C_3N_4 and monolayer BP, respectively. The calculated E_{adh} is -0.50 eV , indicating the

Fig. 1 Optimized geometric structures. Top views of (a) g- C_3N_4 and (b) BP. (c) Top view (upper) and side view (lower) of BP/g- C_3N_4 heterojunction.

Pink, blue and gray spheres represent P, N and C atoms, respectively. Color online.

formation of BP/g-C₃N₄ is an exothermic process, suggesting the composite is thermodynamically stable.

3.2 Electronic properties

To reveal the photocatalytic mechanism in BP/g-C₃N₄ heterojunction, electronic properties were investigated, including the density of states (DOS) and work function of BP and g-C₃N₄, and the charge density difference of BP/g-C₃N₄ composite. The DOS was calculated using HSE06 hybrid functional. As shown in Fig. 2, the calculated band gaps of monolayer g-C₃N₄ and BP are 2.78 and 1.48 eV, respectively, in consistency with the previous experimental and theoretical values^{44,45}. The valence band (VB) of g-C₃N₄ mainly consists of N 2*p* orbital, and the conduction band (CB) of g-C₃N₄ is composed of C 2*p* and N 2*p* orbitals⁴⁶. For BP, both the VB and CB are mainly dominated by P 2*p* orbital.

Work function (Φ) is an important criterion for evaluating electron transfer. It is obtained by calculating the electrostatic potential along Z axis direction and defined as:

$$\Phi = E_{\text{Vac}} - E_{\text{F}} \quad (4)$$

where E_{Vac} and E_{F} represent the electrostatic potentials of vacuum level and Fermi level, respectively. As illustrated in Fig. 3, the computed respective work functions of g-C₃N₄ and BP are 4.28 and 4.54 eV, suggesting that the Fermi level of g-C₃N₄ is higher than that of BP^{42,47,48}. Therefore, it can be deduced that as the two layers incorporate, the Fermi level difference drives electrons transfer from g-C₃N₄ to BP until an equilibrium Fermi level is achieved.

The electron transfer between the two components can be intuitively reflected by charge density difference ($\Delta\rho$), which is calculated based on the following equation:

$$\Delta\rho = \rho(\text{BP/g-C}_3\text{N}_4) - \rho(\text{BP}) - \rho(\text{g-C}_3\text{N}_4) \quad (5)$$

where $\rho(\text{BP/g-C}_3\text{N}_4)$, $\rho(\text{BP})$, and $\rho(\text{g-C}_3\text{N}_4)$ are the charge densities of BP/g-C₃N₄ heterojunction, monolayer BP and monolayer g-C₃N₄, respectively. Fig. 4a,b illustrate the three-dimensional and planar-averaged charge density difference of BP/g-C₃N₄ heterojunction, respectively. In three-dimensional view, the yellow and blue regions represent charge accumulation and depletion, respectively. In planar-averaged curve, the positive and negative $\Delta\rho$ values signify charge density increase and decrease, respectively. In Fig. 4, it is clear that the yellow and blue regions are principally distributed in the interlayer space between BP and g-C₃N₄. As such, the main peak location in planar-averaged curve also provides the same information. These results sufficiently disclose the strong interfacial interaction in BP/g-C₃N₄ heterojunction. Further observation shows that the yellow region is mainly distributed on the surface of BP, and the upper layer of g-C₃N₄ is covered by blue region. Correspondingly, in the planar-averaged curve, the $\Delta\rho$ value is primarily positive and negative at the BP and g-C₃N₄ side, respectively. These finding convincingly demonstrates that the electrons in g-C₃N₄ transfer to BP, in line with work function analysis. The interfacial electron transfer induces the formation of an interfacial built-in electric field, which is conducive to the later migration of photogenerated charge carriers.

Fig. 2 Calculated DOS of monolayer (a) g-C₃N₄ and (b) BP using HSE06 functional.

Fig. 3 Electrostatic potentials of monolayer (a) g-C₃N₄ and (b) BP.

The blue and red dashed lines represent the vacuum level and Fermi level, respectively. Color online.

Fig. 4 (a) Three-dimensional and (b) planar-averaged charge density difference of BP/g-C₃N₄ heterojunction.

The isosurface value is 0.3 e-nm⁻³.

Optical absorption, an important factor, is evaluated by calculating the absorption coefficient using the following formula:

$$\alpha(\omega) = \sqrt{2}\omega \left[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega) \right]^{1/2} \quad (6)$$

where ε_1 and ε_2 represent the real and imaginary parts of the dielectric function, respectively; ω denotes the light frequency. The result is depicted in Fig. 5. In a wide photo energy range of 1.5–4.0 eV, the absorption coefficient follows the order of BP/g-C₃N₄ > BP > g-C₃N₄. Therefore, the hybridization of BP and g-C₃N₄ results in increased light absorption, which is conducive to the photoexcitation of electrons and holes.

3.3 Photocatalytic mechanism

Based on the above electronic properties, the photocatalytic mechanism in BP/g-C₃N₄ heterojunction is discussed. Initially, the band edge potentials are calculated using the following equations:

$$E_{VB} = \chi - E^e + 1/2E_g \quad (7)$$

$$E_{CB} = E_{VB} - E_g \quad (8)$$

where E_{VB} and E_{CB} are the potentials of valence band and

conduction band, respectively. χ is the absolute electronegativity of the semiconductor, and it is 4.34 eV and 5.62 eV for g-C₃N₄ and BP, respectively^{49,50}. E^e is the energy of free electrons on the hydrogen scale (4.5 eV). E_g values of g-C₃N₄ and BP are 2.78 and 1.48 eV, respectively. Therefore, the obtained VB and CB potentials of g-C₃N₄ are 1.23 and -1.55 eV, respectively, and those of BP are 1.86 and 0.38 eV, respectively. The calculated band edge potentials of g-C₃N₄ are higher than those of BP, which is consistent with experimental results^{51,52}. Judging from the results, a staggered band structure is constituted in BP/g-C₃N₄ heterojunction.

Subsequently, the photocatalytic mechanism in BP/g-C₃N₄ heterojunction is proposed and displayed in Fig. 6. After g-C₃N₄ comes into contact with BP, electrons migrate from g-C₃N₄ to BP because of its smaller work function and higher Fermi level. As a result, a built-in electric field pointing from g-C₃N₄ to BP is formed. Meanwhile, as varying degrees of the electronic potentials at different regions, the CB and VB of g-C₃N₄ bend up, and those of BP bend down. Under visible-light irradiation, both g-C₃N₄ and BP are excited to generate electron-hole pairs.

Fig. 5 Optical absorption coefficient of g-C₃N₄, BP, and BP/g-C₃N₄ composite.

Fig. 6 The S-scheme photocatalytic mechanism in BP/g-C₃N₄ heterojunction.

Driven by the collective effect of built-in electric field, band bending, and Coulomb attraction, photogenerated electrons in the CB of BP will combine with the photogenerated holes in the VB of g-C₃N₄. Accordingly, the photogenerated electrons with strong reduction ability in the CB of g-C₃N₄ survive from recombination and energetically participate in CO₂ reduction reaction. Meanwhile, the photogenerated holes in the VB of BP have strong oxidation ability to induce oxidation reaction such as pollutant degradation. The above migration process of charge carriers conforms to the typical S-scheme photocatalytic mechanism^{53,54}. In a word, BP/g-C₃N₄ composite is a S-scheme heterojunction photocatalyst with both efficient charge separation and enough reduction capacity for CO₂ conversion.

3.4 CO₂ reduction reaction process

Typically, CO₂ is converted into a series of products (such as CO and CH₃OH) *via* sequential hydrogenation steps aided by photogenerated electrons^{55,56}. In each step, H atom is added either on C or on O atom, thus resulting in various intermediates. According to the generation of different intermediates, some reaction paths are proposed and illustrated in Fig. 7. In general, the change in Gibbs free energy of each step is calculated and compared to determine the preferential reaction path and maximum energy barrier.

As for the reduction process from CO₂ to CH₃OH on g-C₃N₄ surface, an established reaction path has been acknowledged in many theoretical researches^{57,58}, namely, CO₂ → COOH* → CO → HCO* → H₂CO → H₃CO* → CH₃OH. In view of the fact, we also chose this path to investigate the CO₂ reduction on g-C₃N₄ surface, without considering other reaction paths. Fig. 8a shows the variation of Gibbs free energy in the CO₂ reduction process on g-C₃N₄ surface. As can be seen, three steps with

uphill energy are CO₂ → COOH*, CO → HCO*, and H₂CO → H₃CO*, require energy input of 1.48, 0.19, and 1.12 eV, respectively. By contrast, the other three steps are downhill processes. Hence, the hydrogenation of CO₂ to COOH* with the largest Δ*G* is the rate-determining step, and the corresponding energy barrier is 1.48 eV. Previous reports also concluded that the hydrogenation of CO₂ is the most difficult step in the CO₂ reduction process on many g-C₃N₄-based photocatalytic systems^{58,59}. Fig. 8b shows the optimized geometric structures of the reaction system. It is observed that COOH, HCO, and H₃CO groups are linked with g-C₃N₄ *via* the formation of C—N or O—C bond, while CO₂, CO, H₂CO, and CH₃OH molecules are adsorbed on g-C₃N₄.

Afterwards, the CO₂ reduction process on BP/g-C₃N₄ heterojunction is explored. Prior to the exploration, it should be determined whether CO₂ reduction proceeds on the surface of g-C₃N₄ or that of BP. On the basis of the aforementioned S-scheme photocatalytic mechanism, the photogenerated electrons in the CB of BP are consumed by the photogenerated holes in the VB of g-C₃N₄, while the separated photogenerated electrons in the CB of g-C₃N₄ can trigger CO₂ conversion. In this regard, the CO₂ reduction reaction prefers to occur on the g-C₃N₄ component in BP/g-C₃N₄ composite. Besides, as CO₂ adsorption is influential for the later reduction process, the CO₂ adsorption on both side of BP/g-C₃N₄ heterojunction is compared. Fig. 9 shows the optimized geometric structures. The calculated adsorption energy is −1.57 and −1.47 eV, respectively, manifesting the more stable adsorption on the g-C₃N₄ side. Therefore, the CO₂ reduction on the g-C₃N₄ side of BP/g-C₃N₄ heterojunction is investigated.

Concerning the reduction process of CO₂ to CH₃OH on BP/g-

Fig. 7 Possible reaction paths of CO₂ reduction to CH₃OH.

Fig. 8 (a) Free energy diagram of the reaction system and (b) optimized geometric structures in the CO₂ reduction process on g-C₃N₄ surface.

The red and white balls denote O and H atoms, respectively. Color online.

Fig. 9 Optimized geometric structures of CO₂ adsorption on the (a) g-C₃N₄ side and (b) BP side of BP/g-C₃N₄ heterojunction.

Fig. 10 (a) Free energy diagram of the reaction system and (b) optimized geometric structures in the CO₂ reduction process on BP/g-C₃N₄ heterojunction.

C₃N₄ heterojunction, various reaction paths are examined. As shown in Fig. 10a, in the first hydrogenation step, the formation of COOH* requires a lower energy input of 1.22 eV than that of HCOO*, indicating that CO₂ is firstly reduced to COOH* rather than HCOO*. Then the COOH* is hydrogenated to HCOOH, or converted to CO *via* dehydroxylation. The COOH* → HCOOH step releases energy of 0.88 eV, larger than the COOH* → CO step (0.47 eV). Therefore, HCOOH is a preferential intermediate product than CO. The adsorption energy of HCOOH is −1.92 eV. Subsequently, the HCOOH is further hydrogenated and dehydrated to produce HCO*, and the corresponding free energy is elevated by 1.08 eV. In the following process of HCO* hydrogenation, wide disparity exists between the reaction free energy of H₂CO and CHOH*. The generation of H₂CO is an exothermic process, while the production of CHOH* is an endothermic reaction. Hence, HCO* is more likely to be hydrogenated to H₂CO. The adsorption energy of H₂CO is −1.58 eV. The next-step hydrogenation of H₂CO involves the generation of H₃CO* and CH₂OH*, in which the Δ*G* value is 0.80 and 0.21 eV, respectively. Thus, the final reduction step is continued by the hydrogenation of CH₂OH* to CH₃OH releasing 0.92 eV. The adsorption energy of CH₃OH is −1.71 eV. Overall,

the optimal reaction path of CO₂ reduction on BP/g-C₃N₄ heterojunction is described as CO₂ → COOH* → HCOOH → HCO* → H₂CO → CH₂OH* → CH₃OH. Similarly, on pristine g-C₃N₄, the rate-determining step is also the hydrogenation of CO₂ to COOH* but with a decreased energy barrier from 1.48 to 1.22 eV. The lowered energy barrier indicates a more facile CO₂ reduction reaction process on BP/g-C₃N₄ heterojunction.

Fig. 10b shows the optimized geometric structures of the reaction system corresponding to the optimized CO₂ reduction reaction path on BP/g-C₃N₄ heterojunction. Analogous to the geometric structures on pristine g-C₃N₄ surface, the COOH, HCO, and CH₂OH groups are linked with the g-C₃N₄ component in BP/g-C₃N₄ composite *via* the formation of C–N bond, while the CO₂, HCOOH, H₂CO, and CH₃OH molecules are adsorbed on the g-C₃N₄ side of BP/g-C₃N₄ composite.

4 Conclusions

In summary, geometric structures, electronic properties, photocatalytic mechanism, and CO₂ reduction reaction processes of 2D/2D BP/g-C₃N₄ heterojunction are investigated by DFT calculations. Monolayer BP and g-C₃N₄ constitute a stable BP/g-C₃N₄ composite with negative adhesion energy of −0.50 eV and

moderate equilibrium distance of 0.26 nm. Work function and charge density difference disclose the strong interfacial interaction. The electron transfer between BP and g-C₃N₄ induces the formation of built-in electric field and band bending. As a result, the charge migration in BP/g-C₃N₄ heterojunction follows S-scheme photocatalytic mechanism, and the photogenerated electrons with strong reduction ability are efficiently separated and accumulated in g-C₃N₄. Then the reaction process of CO₂ reduction to CH₃OH on the g-C₃N₄ side in BP/g-C₃N₄ heterojunction is examined. The optimal reaction path is determined as CO₂ → COOH* → HCOOH → HCO* → H₂CO → CH₂OH* → CH₃OH. The hydrogenation of CO₂ to COOH* is the rate-determining step, and the corresponding energy barrier is 1.22 eV. By comparison, the traditional CO₂ reduction reaction path on pristine g-C₃N₄ exhibits a maximum energy barrier of 1.48 eV. Overall, BP/g-C₃N₄ S-scheme heterojunction is featured with efficient charge separation, strong reduction capacity, and facile CO₂ reduction reaction process; it is undoubtedly an outstanding CO₂ reduction photocatalyst.

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