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Cooperative Syngas Production and C–N Bond Formation in One Photoredox Cycle

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Abstract: Solar-driven syngas production by CO₂ reduction provides a sustainable strategy to produce renewable feedstocks. However, this promising reaction often suffers from tough CO₂ activation, sluggish oxidative half-reaction kinetics and undesired by-products. Herein, we report a functionoriented strategy of deliberately constructing black phosphorus quantum dots- $ZnIn_2S_4$ (BP/ZIS) heterostructures for solardriven CO₂ reduction to syngas, paired with selectively oxidative C-N bond formation, in one redox cycle. The optimal BP/ZIS heterostructure features the enhanced chargecarrier separation and enriched active sites for cooperatively photocatalytic syngas production with a tunable ratio of CO/ H_2 and efficient oxidation of amines to imines with high conversion and selectivity. This prominent catalytic performance arises from the efficient electronic coupling between black phosphorus quantum dots and $ZnIn_2S_4$, as well as the optimized adsorption strength for key reaction intermediates, as supported by both experimental and theoretical investigations. We also demonstrate a synergistic interplay between CO_2 reduction and amine dehydrogenation oxidation, rather than simply collecting these two single half-reactions in this dualfunctional photoredox system.

Introduction

Syngas (the mixture of H_2 and CO), a key feedstock for accessing value-added chemicals, has been usually produced by the energy-intensive thermocatalysis process, such as steam reforming of natural gas and gasification of coal.^[1] In contrast, photocatalytic CO₂ reduction reaction (CRR) provides an alternatively sustainable strategy to obtain clean, renewable and storable syngas.^[1b,2] However, this promising photocatalytic reaction is often hampered by the high thermodynamic stability of CO₂ molecules, sluggish oxidative half-reaction kinetics and undesired by-products.^[2] Much research has been devoted to exploring highly efficient photocatalysts toward CRR based on promoting the adsorp-

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tion and activation of inert CO_2 , while few researches have tuned the oxidative half-reaction,^[3] which usually resorts to the hole consumption by diverse sacrificial reagents,^[3c,4] such as triethanolamine (TEOA), ascorbic acid, and sodium sulfite, etc. Notably, as an unwanted by-product in conventional CRR with pure H₂O as the reducing agent, O₂ readily accepts electrons that competes with the CO₂ reduction half-reaction, and produces a series of system-damaging reactive oxygen species after reduction.^[5] Moreover, O₂ has only limited commercial application and is usually associated with costly separation from syngas.^[6]

Replacing the above-mentioned oxidative half-reactions in conventional CRR with valued organic oxidation reactions would avoid O_2 production, and allow the simultaneous use of photogenerated electrons and holes for respective syngas production and value-added chemical synthesis. A promising process is the selective oxidation of amines to imines, which are widely used as intermediates for complex syntheses in the pharmaceutical and fragrance industries.^[5b,7] In addition, amines could act as Brønsted acids providing protons or Lewis bases donating electrons, which can favor the CO₂ adsorption, activation and reduction dynamics,^[8] while CO₂ could be used as a catalyst or mediating reagent for amine dehydrogenation oxidation.^[7,9]

Such a cooperative reaction system requires the effective couplings among the light-harvesting based energy cycle, two redox catalytic cycles and accumulating gaseous/liquid products without opposite interference. The competition of two half-reactions, i.e., CRR and H₂ evolution reduction (HER) from amine dehydrogenation oxidation, greatly impacts the CO/H₂ ratio in syngas mixtures, which is the crucial consideration for different downstream products.^[10] Importantly, the high-rate syngas and imine productions demand the rational ensemble of abundant catalytic sites and high electron-hole separation capability.^[11] Catalysts with low overpotential for CRR and low CO desorption energy are preferential for the highly selective production of syngas and imines. In this context, in contrast to transition metal-based catalysts, which may result in methanation, aminocarbonylation and catalysts poisoning due to their strong HER activity and chemisorption for amines and CO,^[12] nonmetallic elements with abundant valence electrons and weak chemisorption of CO and H₂ could provide ideal active reaction centers for syngas production.

Black phosphorus (BP), a newly emerging two-dimensional (2D) layered metal-free material, has been recently explored for solar energy harvesting and conversion.^[13] In particular, in the unit cell of BP, every P atom has five valence electrons (i.e., $3s^23p^3$ configuration). The electrons in 3p orbital covalently bond with three neighboring P atoms, while

the other two electrons in the 3s orbital are retained.^[14] These lone-pair electrons in the 3s orbital of P atoms or 3p orbital of edge P atoms featuring abundant electron cloud density could attract the electrophilic carbon center of CO₂, thereby weakening the C=O double bonds of CO_2 .^[12c, 15] Recent density functional theory (DFT) studies have also suggested that BP-based materials exhibit stronger adsorption toward acidic gases such as CO₂ than CO and H₂.^[16] Furthermore, the weak van der Waals interaction within BP layered crystal allows bulk BP to be exfoliated into zero-dimensional quantum dots (QDs),^[17] exposing a large number of intrinsic active sites. These inherent structural and electronic features are beneficial for promoting the adsorption and activation of the inert CO₂ molecules. Herein, differing from previous reported BP-based heterostructures for single-functional solar fuel production,^[17a,18] we for the first time report the use of facile electrostatic interaction assembly method to anchor BP QDs onto the surface of 2D ZnIn₂S₄ nanosheets (ZIS NSs) to synthesize BP QDs-ZnIn₂S₄ (BP/ZIS) heterostructures, and demonstrate their application as functionoriented photocatalysts toward simultaneous and efficient use of electrons and holes to cooperatively produce syngas and value-added C-N coupling organics under visible light irradiation.

Results and Discussion

We chose BP QDs and ZIS NSs to construct the heterostructures due to their efficient visible light response and matched band alignment. In addition, the thermodynamic feasibility of ZIS for either CO2 reduction or chemical dehydrogenation oxidation has been well demonstrated.^[19] Firstly, few-layer BP QDs were exfoliated from bulk BP (Figure S1a) by a solvothermal method in the solvent of Nmethyl-2- pyrrolidone (NMP).^[17b,c] The absorption spectrum of BP QDs solution shows a broadband absorption in the ultraviolet-visible (UV-vis) region (Figure S1b). The optical band gap (E_{a}) of the BP QDs is estimated to be approximately 2.30 eV (inset of Figure S1b), consistent with the previous report.^[20] The as-obtained BP QDs dispersed in the NMP solvent show a clear blonde phase, which can store at room temperature for more than one month without obvious aggregation, as confirmed by the Tyndall effect (Figure S1c). The transmission electron microscopy (TEM) images (Figure S2a,b) suggest that the average lateral size of BP QDs is about 5.6 nm. Atomic force microscopy (AFM) analyses (Figure S2c,d) disclose that the thickness of BP QDs (3.5-6.2 nm) is closed to that of the 5-12 phosphorus atomic layers based on the monolayer thickness of 0.5-0.7 nm.[21] Raman spectra of BP QDs show three characteristic peaks corresponding to the out-of-plane phonon mode A_g¹, in-plane phonon mode B_{2g} and in-plane phonon mode A_g² (Figure S3).^[14,17c] Compared to bulk BP, these peaks are all shifted to high wavenumber, confirming the successful exfoliation of BP QDs from bulk BP.^[20] Blank ZIS NSs were prepared through a hydrothermal synthesis process.^[22] Scanning electron microscope (SEM) image (Figure S4a), TEM images (Figure S4b,c) and AFM analyses (Figure S4d,e) show that

bare ZIS is layered structure and relatively flat with an average thickness of 3.1 nm, which approximately corresponds to two Zn-In-S molecular layers.^[23]

The overall preparation process for the BP/ZIS hybrids is shown in Figure 1a, which mainly involves the separate preparation of ZIS NSs and poly(diallyldimethylamonium chloride) (PDDA) functionalized-BP QDs, followed by an electrostatic assembly of PDDA functionalized BP QDs (PDDA-BP QDs) on the surface of ZIS.^[14,24] As shown in Figure 1b, the bare ZIS and BP QDs are negatively charged with a zeta potential of -43 and -37 mV, respectively. To ensure the electrostatic attraction, positively charged PDDA-BP QDs were prepared, which have a zeta potential of +38 mV. After liquid-phase mixing of ZIS with a certain amount of PDDA-BP QDs under the assistance of sonication and stirring (Figure S5), the BP/ZIS composites with different loading amount of BP QDs (denoted as xBP/ZIS, x defines as the weight percentage of BP QDs) were obtained. Figure 1c,d show the overview TEM images of the as-prepared 8BP/ZIS heterostructure that displays the optimal photocatalytic activity as shown below. Compared with the smooth surface of bare ZIS NSs (Figure 1e), it is clearly seen that BP QDs are uniformly dispersed on the surface of ZIS. High-resolution TEM (HRTEM) images (Figure 1 f and Figure S6) display the distinct lattice fringes with d-spacings of 0.33 and 0.21 nm, corresponding to the (101) plane of ZIS and (002) plane of BP QDs, respectively.^[17b] Furthermore, the energy-dispersive Xray spectrum (EDS, Figure S7) and the elemental mapping images (Figure 1g) indicate the presence of In, Zn, S and P elements in the 8BP/ZIS composite and the uniform distribution of element P on the surface of ZIS.

Ultraviolet-visible-near infrared (UV-vis-NIR) diffuse reflectance spectroscopy (DRS) was employed to explore the optical absorption capacities of different samples. As disclosed in Figure 2 a, the bare ZIS shows a light absorption threshold at 534 nm, corresponding to their intrinsic band gap of 2.32 eV;^[22] while for the BP/ZIS samples, a slight shift of absorption threshold can be detected. Notably, with the increase of the weight percentage of BP QDs loading, the absorption intensity of the BP/ZIS heterostructures is significantly enhanced in the wavelength of $\lambda > 500$ nm vis-NIR region. However, excess BP QDs loading on the panel of ZIS NSs will inhibit the intrinsic band gap absorption of ZIS due to the photon scattering effect of BP.^[25]

X-ray diffraction (XRD) analysis was performed to further detect the crystal structure and phase information of the samples. As shown in Figure 2b, the pure ZIS sample shows several diffraction peaks located at $2\theta = 21.7, 28.0, 39.8,$ 47.3, 52.7 and 55.7°, which can be attributed to the (006), (102), (108), (110), (116) and (022) lattice plane of the hexagonal ZIS (JCPDS No. 72-0773),^[26] respectively. The BP/ ZIS hybrids with different BP QDs loading contents show a similar hexagonal structure to pristine ZIS. Except for 10BP/ZIS sample, which gives two additional peaks assigned to hexagonal structured BP, no evident difference in the peak intensity or position can be detected in other BP/ZIS hybrids. This result indicates that the basic structure of ZIS is preserved during the mild preparation process. Figure 2c shows the Raman spectra of pristine ZIS and BP/ZIS hybrids.



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Figure 1. a) Schematic preparation of BP/ZIS composites. b) Zeta potentials of blank ZIS, BP QDs, and PDDA-BP QDs. TEM images of c,d) 8BP/ZIS composite and e) blank ZIS NSs. White circles in d) indicate the BP QDs. f) HRTEM image and g) elemental mapping results of 8BP/ZIS composite.

As for pristine ZIS, the band at about 123 cm⁻¹ confirms its layered structure.^[27] The other three characteristic Raman peaks at about 92, 242 and 345 cm⁻¹ can be ascribed to the F_{2g} , LO₁ and LO₂ optical modes of ZIS, respectively.^[28] In comparison with pristine ZIS, no distinct shift can be observed for these peaks in 2BP/ZIS and 4BP/ZIS heterostructures with relatively low BP QDs loading content. In the cases of 8BP/ZIS and 10BP/ZIS, the F_{2g} peak slightly shifts to low wavenumber compared with that of ZIS, indicating the possible electron transfer across the BP/ZIS interface.^[26] The additional three peaks in 10BP/ZIS located at 360, 437, and 465 cm⁻¹ are assigned to A_g^1 , B_{2g} and A_g^2 vibration modes of BP, respectively.^[17c]

The chemical composition and oxidation states of 8BP/ ZIS hybrids were determined by X-ray photoelectron spectroscopy (XPS). The wide-scan survey XPS spectrum in Figure S8 shows the presence of the characteristic lines of the constituent elements Zn, In, S and P in the sample of 8BP/ ZIS. The high-resolution XPS spectra (Figure S9) suggest that as compared to bare ZIS, the peaks of S 2p, In 3d and Zn 2p in 8BP/ZIS slightly shift toward higher binding energy, which further reveals the electronic communication between BP QDs and ZIS in BP/ZIS hybrids.^[29] The P 2p spectrum (Figure S9d) exhibits the $2p_{3/2}$ and $2p_{1/2}$ doublet at 129.7 and 130.7 eV, respectively, which are the characteristic features of the P-P bonds.^[30] The broad peak corresponding to P_xO_y species at ca. 136.1 eV arises from the inevitable oxidation during the sample preparation and characterization of XPS analysis.^[31] Based on the quantification from the XPS analysis, the loading content of P on the surface of 8BP/ZIS hybrid is calculated to be 7.4 wt %.

In the next, the photocatalytic assay of as-prepared BP/ ZIS composites toward CO₂ reduction coupled with benzylamine (BA) dehydrogenation oxidation was evaluated under visible ($\lambda > 420$ nm) light irradiation. As is clearly seen, compared to bare ZIS, the production rates of CO (Figure 2d) and N-benzylidenebenzylamine (BDA, Figure 2e), and the conversion of BA (Figure 2e) over the BP/ZIS



Figure 2. a) DRS, b) XRD and c) Raman spectra of blank ZIS and BP/ZIS composites with different BP QDs loading contents. d) H_2 , CO production rates, e) BA conversion and BDA production rate in the photocatalytic CO₂ reduction paired with selective BA oxidation under visible light ($\lambda > 420$ nm) irradiation of 1 h over blank ZIS and BP/ZIS composites with different BP QDs loading contents. f) Long-term photoactivity of CO₂ reduction paired with selective BA oxidation over 8BP/ZIS composite.

composites exhibit obviously increasing trends, while it is worth noting that the production rate of H₂ (Figure 2d) is nearly unchanged. In addition to CO, no detectable CH₄, CH₃OH and HCOOH are observed. In the absence of light or photocatalyst, no CO and H₂ can be detected, and only trace amounts of BDA are produced (Figure S10). These results suggest that the cooperative syngas production and C–N bond formation reactions are indeed driven by the light-harvesting of BP/ZIS composites. Interestingly, the results show that with the variation of loading content of the BP QDs, the CO/H₂ ratio (Figure S11) can be adjusted in a large range, including 1:2 and 1:3, which are the desirable composition of syngas mixtures for methanol and methane production, respectively.^[2a,10a,12a]

Notably, it was found that 8BP/ZIS is the optimum photocatalyst to achieve the highest conversion of BA and the maximum production rate of syngas. When the BP QDs loading content exceeds 8 wt %, the photocatalytic efficiency is decreased. This could be ascribed to the photon scattering effect of BP QDs^[25] that blocks the light absorption of ZIS in 10BP/ZIS composite (Figure 2a). The long-term photoactivity test over 8BP/ZIS in Figure 2 f shows that the production rates of H₂ and CO increase along with the prolonged reaction time. After 4 h of irradiation, the conversion of BA is about 95.1% and the selectivity for BDA reaches 94.0%. No other by-products, such as benzonitrile and N-benzylformamide, which are usually involved in O2 or CO2-catalytic oxidation of BA,^[32] can be detected by gas chromatography-mass spectrometry (GC-MS) analysis (Figure S12), indicating the high selectivity toward BDA. The H₂ and CO productions are 27.2 and 15.0 µmol, respectively, with an apparent quantum yield (AOY) of 6.5% at 465 nm. In addition, the CO/H₂ ratio in syngas mixtures can be tuned over a wide range between 1:6 and 2:3 by adjusting the concentration of substrate BA (Figure S13). The photocatalytic performance of 8BP/ZIS is also comparable to other homogeneous and metal-semiconductor heterojunction-based reaction systems toward BA oxidation (Table S1). Furthermore, the results of recycling test, as well as the characterizations of the fresh and used samples (Figure S14) suggest the good stability of 8BP/ZIS.

To study the stoichiometry of this reaction, the ratios of the oxidation product (i.e., BDA) and reduction products (i.e., H₂ and CO) were calculated (Table S2). The results show that the production rate of BDA is slightly higher than the total rate of H₂ and CO production, which can be ascribed to the adsorption of H species on the surface of catalysts, as reflected in the color change of the samples shown in Figure S15.^[19c] The trace amount of CO production in a controlled experiment with the Ar atmosphere (Figure S16) and isotope-labeling measurement by using ${}^{13}CO_2$ as the feedstock (Figure S17) also suggests that the CO is derived from CO₂ instead of organic carbonaceous impurities. In addition, the photoactivity under standard conditions is even higher than that of using TEOA or Na₂SO₃ as sacrificial reagents (Figure S16). Controlled experiments without BA or with BDA as hole scavenger show almost no syngas production (Figure S16). These results, as well as the isotopic experiment with deuterated-BA as hole scavenger (Figure S18), indicate that BA serves as both electron and proton donors. It is worth noting that the production rates of both oxidation and reduction products are significantly decreased when the reactor is purged with Ar instead of CO₂. Especially, the BDA production rate in the CO₂ atmosphere is more than twice as much as that in Ar saturated condition. We also



checked the pH of different reaction systems, and the results show that the pH factor is not the predominant effect influencing the CO/H_2 ratio (Table S3). The above results suggest a synergistic interplay between CO_2 reduction and BA oxidation.

In addition to the conventional deprotonation process (path 1 in Figure 3 a), it has been demonstrated that CO_2 can catalytically oxidize amines to imines through $\cdot CO_2^-$ radical anion,^[7] formate (HCOO⁻)^[33] or benzylcarbamic acid intermediates.^[34] However, the reduction of CO_2 to $\cdot CO_2^-$ requires a significant redox potential of -1.9 V vs. NHE (normal hydrogen electrode),^[3c,35] which is more negative than the conduction band bottom (E_{CB}) of ZIS (-0.89 V, as will be discussed below). Therefore, it is difficult to interpret the above reactions through $\cdot CO_2^-$ radical anion. The redox potential of CO₂ to HCOOH (-0.61 V vs. NHE) is more positive than the E_{CB} of ZIS, indicating the feasibility of formate production. However, our DFT calculation results show that the energy barrier involved in this process is relatively large (Figure S19). Thus, we suppose that the BA reacts with CO₂ and produces benzylcarbamic acid intermediate, which shows better electron donor property, thus promoting the redox recycle (path 2 in Figure 3a, see Figure S19 for more details).^[34] Additionally, benzylcarbamic acid intermediate was also successfully detected (Figure S20).

Considering the full extent of details related to this dualfunctional photoredox system, we summarized the overall photocatalytic process in Figure 3 a. The released protons and electrons of dehydrogenation oxidative half-reaction can be

further used for CO₂ reduction, while the CO₂ promotes the BDA and syngas productions. This collaborative approach in the dual-functional photocatalytic system results in higher efficiency than the sacrificial reagent bearing system. Inspired by these results, the scope of the substrates was checked by oxidation of other amines with different substituent groups. Table S4 discloses the performance of CO₂ photoreduction paired with various amine oxidation reactions. It can be seen that the aromatic amines substituted with an electrondonating group give higher conversion and syngas production rates. Interestingly, the dehydrogenative coupling of aliphatic amines is also realized. Compared with primary amines, the secondary amines show much slower reaction rates, which is probably due to the blocking of the CO2-mediated amine oxidation pathway. These results indicate that the efficiency of photocatalytic CRR can be further tuned by optimizing the oxidative half-reaction.

In the next stage, it is highly desired to explore the specific roles of BP QDs in tuning the activity and selectivity of the BP/ZIS composites in the present photocatalytic coupling reaction system. The relative band locations of ZIS and BP QDs were measured via the ultraviolet photoelectron spectra (UPS) technique. The UPS spectra of ZIS and BP QDs are shown in Figure S21a and b, respectively. Based on the linear intersection method,^[36] the maximum valence band ($E_{\rm VB}$) of ZIS and BP QDs are respectively estimated to be 1.43 and 1.63 V (vs. NHE), after subtracting the excitation energy of Helium lamp (21.22 eV). Then, the $E_{\rm CB}$ can be determined by $E_{\rm CB} = E_{\rm VB} - E_{\rm g}$. Based on these results, the band alignments of



Figure 3. a) Schematic of photocatalytic CO₂ reduction paired with selective BA oxidation for the production of syngas and CN coupling chemicals. b) Calculated electron density differences ($\Delta\rho$) upon BP QDs loading on ZIS. $\Delta\rho = \rho(BP/ZIS) - \rho(BP) - \rho(ZIS)$. Gray and black areas represent charge increase and reduction, respectively. The cutoff of the density-difference isosurfaces equals 0.001 electrons Å⁻³. c) PL emission spectra of blank ZIS and 8BP/ZIS composite with an excitation wavelength of 380 nm. d) TRPL decay spectra of blank ZIS and 8BP/ZIS composite. The inset shows the decays dynamics analysis results. e) Photocurrent density versus time (*I-t*) curves and f) electron lifetime calculated from the OCP decay analysis of blank ZIS and 8BP/ZIS composite.

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ZIS and BP QDs are schematically illustrated in Figure S21c and d. Given the matchable band alignment, it is reasonable to form a conventional type II heterojunction between ZIS and BP QDs. Theoretically, the electrons in $E_{\rm CB}$ of ZIS could transfer to BP QDs across the interface of heterojunction. We also simulated the heterojunction interface between ZIS and BP QDs and further calculated the electron density distribution (Figure 3 b). The Mulliken charge transferred from ZIS to BP QDs is $0.33 \, \text{e}^-$, leading to the efficient interfacial charge carrier separation in the composite of BP/ZIS.

Figure 3c shows the steady-state photoluminescence (PL) spectra of pristine ZIS and 8BP/ZIS composite. The broad emission peak ranging from 400 to 500 nm is assigned to the different localized resonant vacancy states in the CB, while the peak centered at about 530 nm is derived from the bandto-band transition of ZIS.^[19c,37] As compared to pristine ZIS, the PL intensity for band-to-band transition in the spectra of 8BP/ZIS is greatly decreased, which can be interpreted by the more efficient charge separation in BP/ZIS heterojunctions.^[17a] To evaluate the decay kinetics of photogenerated charge carriers, time-resolved photoluminescence (TRPL) studies were performed. The TRPL traces were fitted using a biexponential function, and their lifetimes (τ_i) , average lifetimes (τ_A) , amplitudes (A_i) and charge transfer rate constants (k) were calculated according to Equations (1)–(3) and displayed in Figure 3d.^[38]

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$
(1)

$$\tau_{\rm A} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \tag{2}$$

$$k = \frac{1}{\tau_A}$$
(3)

The TRPL traces are dominated by a short lifetime component (τ_1) caused by the defect states emission, followed by a long lifetime component (τ_2) originated from charge carrier recombination within the samples.^[19] It can be clearly seen from the inserted table in Figure 3 d that both single lifetimes and an average lifetime of 8BP/ZIS are shorter than that of pristine ZIS. Consequently, the charge transfer rate constant of *k* over 8BP/ZIS is four-times higher than that of ZIS. The obvious PL quenching and enhanced charge transfer rate suggest the fast separation and migration of photogenerated charge carriers within BP/ZIS composites.^[36a,39]

The enhanced charge carrier separation and migration processes over 8BP/ZIS as compared to pristine ZIS can be further understood by the photoelectrochemical characterizations. As shown in Figure 3 e, the transient photocurrent responses over different electrodes indicate that constructing BP/ZIS heterojunctions is conducive to improving the photocurrent intensity of semiconductor ZIS under visible light illumination.^[40] The open-circuit photovoltage (OCP, Figure S22) and corresponding decay (Figure 3 f) analysis show that 8BP/ZIS discloses a longer electron lifetime than pristine ZIS, because the recombination of electron-hole pairs is prohibited by the enhanced charge separation between two semiconducting phases.^[41] The trend of enhanced interfacial charge carrier separation and migration is also in accordance with the electrochemical impedance spectroscopy performances of the samples (Figure S23).

Notably, the efficient charge carrier separation can not guarantee the high activity and selectivity in CRR. Especially, the adsorption/desorption properties, CO₂ activation and active site issues of photocatalyst also greatly affect the pathway and dynamics of CO₂ photoreaction reduction.^[11,35,41a] To decode the function-oriented effects of BP QDs in promoting photoreduction of CO₂ to CO, CO₂ adsorption and CO desorption performance over the samples were further monitored. The CO2/CO temperature-programmed-desorption (TPD) analyses declare that 8BP/ZIS exhibits stronger CO₂ desorption peak at the range of 50-500°C (Figure 4a), suggesting that BP/ZIS with more adsorption sites largely favors CO₂ adsorption,^[42] which can ultimately offer more opportunities for the electrons to trigger CO₂ reduction at the surface of the catalyst.^[43] On the other hand, the intensity of CO desorption peak over 8BP/ ZIS is evidently stronger and shifted to the lower temperature, as compared to that over pristine ZIS, indicating that the adsorbed CO₂ could be more easily reduced into CO in the presence of H₂ over BP/ZIS sample.^[42,44] Spectroscopic characterizations further confirm the interaction between CO₂ molecules and BP/ZIS surface. As sown in Figure 4b, the PL intensity of 8BP/ZIS in CO₂ saturated solution is significantly decreased compared to that in Ar saturated solution. On the contrary, the UV-vis absorption spectra disclose a negligible change in different solutions, indicating the adsorption of CO₂ does not have substantial impacts on the electronic structure of 8BP/ZIS.^[3c, 16b] Thus, the decreased PL intensity can be ascribed to the adsorption of CO₂ on the 8BP/ZIS surface, which quenches the PL emission by trapping the excited electrons.^[45]

Figure 4c shows that linear sweep voltammetry (LSV) measurements performed over pristine ZIS and 8BP/ZIS composite electrodes in the BA solution saturated with Ar or CO₂. To eliminate the effects of photo-driven charge transfer on current density and overpotential measurements of heterojunction, the LSV tests were conducted under dark condition. In the Ar atmosphere, significant cathodic current ascribing to H₂ evolution is observed at potentials more negative than -0.7 V for both 8BP/ZIS and ZIS electrodes. No obvious difference can be found in the overpotential of H₂ production between these electrodes. After bubbling CO_2 into the electrolyte solution, the reduction products of H_2 and CO can be detected, and a higher cathodic current is observed for both 8BP/ZIS and ZIS electrodes. This result demonstrates that the paired redox reactions became much more efficient under the CO₂ atmosphere, further suggesting the possibility of CO₂ participating in the reaction of dehydrogenative oxidation of BA. In addition, the Tafel plots (Figure S24) suggest that the overpotential of H₂ production for 8BP/ZIS and ZIS electrodes is almost identical, while the overpotential of CO2 reduction over 8BP/ZIS electrode is decreased as compared to ZIS.^[9,46] The controlled-potential CO₂ electrolysis experiments (Table S5) indicate that in contrast to ZIS electrode, the CO production and CO/H₂ ratio over 8BP/ZIS electrode increase significantly with varying the applied potential from -0.5 to -0.9 V. These **Research Articles**



Figure 4. a) CO₂-TPD and CO-TPD analyses over blank ZIS and 8BP/ZIS composite. b) UV-vis absorption spectra and PL spectra of 8BP/ZIS in Ar or CO₂ saturated 20 mM BA acetonitrile solution. c) LSV curves of blank ZIS and 8BP/ZIS composite electrodes under Ar or CO₂ atmospheres. d) Free energy change (ΔG) calculated for CRR via the *COOH intermediate on ZIS (black line) and BP/ZIS (red line). Insets show the side views of optimized geometries of CO₂ and COOH on ZIS and BP/ZIS. e) Charge density difference of *COOH adsorption on ZIS (bottom) and BP/ZIS (top). $\Delta \rho = \rho$ (*COOH/slab)- ρ (slab)- ρ (*COOH), where gray region is charge density increased. f) ΔG calculated for the HER via the *H intermediate on ZIS (black line) and BP/ZIS (red line). Insets show the side views of optimized geometries of *H on ZIS and BP/ZIS.

results combining with the enhanced cathodic current intensity in LSV test suggest that BP QDs could create active sites for regulating the product selectivity in CRR.

DFT calculations were adopted to in-depth understand the heterojunction effect on tuning the selectivity of syngas. The CO₂ reduction to CO has been suggested to proceed via the following sequential steps (Figure 4 d): $^{[2a,3c]}$ 1) CO₂ + * \rightarrow $*CO_2; 2) *CO_2 + H^+ + e^- \rightarrow *COOH; 3) *COOH + H^+ + e^ \rightarrow$ *CO + H₂O; 4) *CO \rightarrow CO + *, where * denotes surface adsorption species/sites. In this case, the adsorption of CO_2 is dominated by physical adsorption, thus chemically adsorbed intermediate *COOH is key species for the CRR.^[45,47] On pure ZIS surface, the chemical bond between surface S and C of *COOH is too strong to break. Therefore, the free energy change (ΔG) calculated from *COOH to CO is as high as +0.69 eV. In contrast, the BP QDs provide a moderate adsorption site for *COOH. On the coordinated unsaturated edge P sites, the free energy change of desorption of *COOH to CO is only +0.16 eV, which is much lower than pure ZIS. The charge density difference of *COOH adsorption on ZIS and BP/ZIS (Figure 4e) also suggests that the charge density change of C-S is more significant than that of C-P, indicating more stronger chemical bond formed between *COOH and blank ZIS. These theoretical results reasonably account for the experimental findings of only H₂ production instead of CO over blank ZIS, and the presence of BP QDs contributing to the formation of CO over BP/ZIS.

DFT calculations were further performed to compare the *HCOO pathway (Figure S25) with *COOH pathway (Figure 4d) in CRR. The results suggest that on the surface of BP/ ZIS, the adsorption energy of *HCOO intermediate (0.02 eV) is very close to that of *COOH intermediate (0.05 eV), indicating that they may compete with each other during the CRR reaction. Both energy barriers of these two reaction pathways are sufficiently low, suggesting that they can proceed smoothly. However, on the pure ZIS surface, a large endothermic energy of 0.83 eV occurs in the rate-determining step of *HCOO formation. On the contrary, the energy change on BP/ZIS surface is only 0.25 eV, which is much more moderate than that on pure ZIS surface. These DFT calculation results jointly imply that the BP/ZIS is more beneficial for the generation of CO through both *COOH and *HCOO pathway.

Considering H₂ is an important component in syngas mixtures, we also calculated the ΔG for HER over blank ZIS and BP/ZIS composite (Figure 4 f). The binding energy of *H reaction intermediate on ZIS is 0.92 eV. Due to this strong *H binding, the adsorption and formation of *COOH and *HCOO are no longer favorable, and thus quenching the CRR.^[47] In contrast, the binding energy of *H on BP/ZIS is much weaker (0.24 eV). This moderated adsorption energy is compatible with that of *COOH and *HCOO, resulting in the smooth production of key reaction intermediates related to CRR.^[48] The above DFT calculations suggest that the BP QDs are able to improve the CRR performance of BP/ZIS composite through optimizing the adsorption energies of *H, *COOH and *HCOO intermediates on the surface of photocatalyst. For the syngas production in alkaline or neutral solution, the hydrophobic surface of BP,^[49] as well as the unique E_{CB} of BP that is closer to the redox potential of CO₂to-CO reduction than that of H₂ evolution,^[18a,50] may further contribute to the promoted kinetics of CO production.

Conclusion

In summary, we reported a dual-functional reaction system for solar-driven CO₂ reduction to syngas paired with selective amine dehydrogenation oxidation in one photocatalytic redox cycle. The function-oriented effects of BP/ZIS for syngas production result from the heterojunction engineering of BP QDs on the surface of ZIS, which promote charge carrier separation, enrich active sites and optimize adsorption strength of key reaction intermediates for CO₂ reduction. Mechanistic studies showed that the cooperative photoredox manner of simultaneous use of electrons and holes also contributes to the markedly enhanced performance of BP/ZIS heterostructures for coproduction of syngas and C–N coupling organics. It is hoped that this work could open a new horizon for exploring novel heterogeneous photocatalysts based cooperative photoredox systems toward more efficient and simultaneous use of electron-hole pairs for solarto-chemical energy conversion to value-added fuels and organic chemicals.

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Conflict of interest

The authors declare no conflict of interest.

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