Nonmetallic plasmonic heterostructures with multi-synergies on boosting hot electron generation for CO2 photoreduction

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Abstract

Constructing multi-physical effects on semiconductors is one new horizon to develop next-generation photocatalysts. Here we use pyroelectric black phosphorus (BP) to couple with nonmetallic plasmonic tungsten oxides (WO) forming a BP/WO heterostructures as photocatalysts to convert CO$_2$ for CO under visible-near-infrared (Vis-NIR) light irradiation. Nonmetallic plasmonic heterostructures exhibit 26.1 µmol h$^{-1}$ g$^{-1}$ CO generation with a selectivity of 98 %, and which is 7- and 17-fold higher than those of plasmonic WO and pyroelectric BP, respectively. The interface P-O-W bonds in heterostructures are constructed to work as channels for electron transfer from BP to plasmonic WO. Moreover, the photothermal energy generated by SPR excitation on WO can make the temperature of heterostructures rapidly increasing from 24 to 86 °C in 10 min, triggering the pyroelectric BP for carriers to promote electron transfer. Multi-physical effects including plasmonic hot carriers and photothermal effect of WO, intrinsic band excitation and pyroelectric effect of BP and W-O-P bonds play synergistic roles on boosting hot electron generation for CO$_2$ reduction. This work provides clear proofs to demonstrate that constructing multi-physical effects on semiconductors is one useful strategy to promote NIR-harvesting for artificial photosynthesis.

Introduction

As the free carrier density reaches $10^{18}$-$10^{21}$ cm$^{-2}$, the surface plasmon resonance (SPR) generally observed on noble metals also occurs on semiconductors such as Cu$_{2-x}$S$_x$, MoO$_{3-x}$, WO$_{3-x}$, and Bi$_2$O$_{3-x}$. Contrast to the metals, nonmetallic plasmonic semiconductors have more complex electronic structures including intrinsic band gap, defect and SPR states, resulting in a complex excitation process and a broad light response in visible-near-infrared (Vis-NIR) region. Currently, the most reported semiconductors with Vis-NIR SPR absorption are focused on heavily oxygen-vacancy- or cation-vacancy-doped metal oxides, and the heavy doping is a valuable strategy to increase semiconductors’ carrier density, resulting in their metalloid properties on optics and catalysis. Taking plasmonic WO$_{3-x}$ as an example, the free-electron on heavy-oxygen-vacancy-doped WO$_{3-x}$ is excited by SPR to be hot electron for catalysis, meanwhile, the consumed electrons are supplied by the intrinsic band gap excitation or electron injection from other semiconductors for maintaining the free carrier density and SPR during photocatalysis. However, the short lifetime of hot carriers on plasmonic semiconductors leads to fast nonradiative decay for photothermal energy, and it restricts the hot electron generation for photocatalysis. Therefore, the synergistic utilization of photothermal effect and hot carriers is one promising strategy to break the above limitations of plasmonic semiconductors for high-efficient photocatalysis.

The pyroelectric effect is one physical phenomenon to convert thermal energy for electrical energy, and which is triggered on crystal materials with non-centrosymmetric structures and has significant applications on pyroelectric nanosensors, electrical generators, and pyroelectric catalysis. Recently,
a pyroelectric-effect-induced electrical field was used to enhance photo-carriers separation in photocatalyst\textsuperscript{32,33}. A ternary heterostructure of poly (vinylidene fluoride-co-hexafluoropropylene (PVDFHFP)/carbon nanotube (CNT)/CdS were reported with the triple functions of pyroelectric, photothermal material and photocatalyst, and in which the pyroelectric-effect-induced electrical field was demonstrated to promote carrier migration and separation for photocatalysis\textsuperscript{33}. Therefore, constructing pyroelectric effect on plasmonic semiconductors will be a new direction for exploring high-efficient photocatalysts. Among various pyroelectric materials, two-dimensional (2D) layer black phosphorus (BP) with broken structure by the loss-of-inversion symmetry exhibits excellent pyroelectric effect and can realize pyro-catalytic H\textsubscript{2} generation under cold-hot alternation\textsuperscript{34}. Owning narrow band gap and pyroelectric effect\textsuperscript{35–37}, 2D BP is one ideal material to marry with plasmonic semiconductors forming heterostructures, and in which multi-physical effects may play synergistic roles on photocatalysis.

In this work, 2D structed BP with pyroelectric effect is coupled with plasmonic tungsten oxides (WO\textsubscript{3}) to form heterostructures as photocatalysts for CO\textsubscript{2}-RR. Under Vis-NIR irradiation, the nonmetallic plasmonic BP/WO heterostructures generate 26.1 µmol h\textsuperscript{−1} g\textsuperscript{−1} CO with a selectivity of 98 %, and which is 7- and 17-fold higher than those of plasmonic WO and pyroelectric BP, respectively. The interface W-O-P bonds to connect WO and BP are demonstrated by density functional theory (DFT) calculations and verified by various spectroscopic studies to work as electron transfer channels between BP and WO. Moreover, the pyroelectric effect of 2D BP can be triggered by photothermal energy from plasmonic WO for carriers to promote electron transfer. Therefore, multi-physical effects on BP/WO heterostructures including plasmonic photothermal effect and hot carriers of WO, intrinsic band excitation and pyroelectric effect of BP and W-O-P bonds play synergistic roles on boosting hot electron generation for high-selective CO generation. This work provides one useful strategy to promote photocatalytic performance of plasmonic semiconductors by constructing synergy of multi-physical effects on heterostructures.

Results

Samples characterization. Layered BP and WO\textsubscript{3}–x (WO) were synthesized by previous reported methods\textsuperscript{38,39}, and their layer and nanowire morphologies were shown in TEM images (Supplementary Figs. 1a-d), respectively. HR-TEM images (Supplementary Figs. 1b and 1d) show the 0.26 and 0.38 nm lattices spacing assigned to \{040\} facets of BP layers\textsuperscript{40} and \{010\} facets of W\textsubscript{18}O\textsubscript{49} nanowires\textsuperscript{41}, respectively. BP/WO heterostructures were synthesized by using simple mixing in solution under ultrasonication, and TEM images (Figs. 1a and b) showed the structures of 10-BP/WO with 10 wt% BP in composition. The 0.38 and 0.26 nm lattice spacing assigned to WO nanowires and layered BP are observed on HR-TEM image (Fig. 1c) of 10-BP/WO heterostructure. The constructed heterostructures were further characterized by the scanning TEM (STEM) coupled with energy-dispersive x-ray spectroscopy (EDX). The high-angle annular dark-field (HAADF) STEM image (Fig. 1d) shows the different contrast on the positions of nanowires and nanosheets in the heterostructures. Meanwhile, the distributions of P, O and W elements are labeled in EDX mapping images (Fig. 1e-h). O and W atoms are mainly located on nanowires, while, P atoms are located on nanosheets, verifying the BP/WO heterostructures. Crystal
structures of BP/WO heterostructures were characterized by x-ray diffraction (XRD, Supplementary Fig. 2), and their XRD patterns are consistent with those of BP and WO without any other peaks.

UV-Vis-NIR diffuse reflectance spectra (DRS, Fig. 1i) shows the optical properties of different samples. 2D BP has a narrow band gap and a broad light response in visible region, and WO nanowires exhibit strong SPR absorption in Vis-NIR region. 10-BP/WO heterostructure has a similar SPR band with that of WO, and the slight enhancement UV-Vis absorption is attributed to 10 wt% BP loading. Chemical structures of 10-BP/WO were analyzed by Raman spectra (Supplementary Fig. 3) and Fourier transform infrared (FTIR) spectra (Supplementary Fig. 4). Weak signal of P-O-W bonds was detected at 1116 cm$^{-1}$, indicating that a small amount of P-O-W bonds exist on interface to connect WO and BP$^{42,43}$. Oxygen vacancies in 10-BP/WO heterostructures and plasmonic WO were detected by electron paramagnetic resonance (EPR) spectra and similar concentrations were observed in Fig. 1j$^{[44]}$. X-ray photoelectron spectra (XPS) show the chemical state of elements in different samples. For BP, XPS of P 2p (Fig. 1k) are deconvoluted into two 129.5 and 130.4 eV bands, assigned to 2p$_{3/2}$ and 2p$_{1/2}$, respectively$^{45}$, and another bond at 133.5 eV is attributed to the oxidized phosphorus (P$_x$O$_y$)$^{46}$. While, the bands of P 2p$_{3/2}$ and 2p$_{1/2}$ on 10-BP/WO heterostructure have 0.5 eV shift toward high binding energy direction, implying the decreased electronic affinity on BP. XPS of W 4f on WO (Fig. 1l) show two broad bands which can be divided into four bands with binding energy of 35.1, 37.1, 36.1 and 38.1 eV assigned to W$^{5+}$ 4f$_{7/2}$, W$^{5+}$ 4f$_{5/2}$, W$^{6+}$ 4f$_{7/2}$, and W$^{6+}$ 4f$_{5/2}$, respectively$^{47}$. The W$^{5+}$ is generated from the W$^{6+}$ reduction during the solvothermal process. For 10-BP/WO, W 4f bands have a 0.1 eV shift toward low binding energy direction, showing the increased electron affinity on WO. Those results indicate the electrons transfer from BP to WO. P = O and P-OH bonds in 10-BP/WO were detected by O 1s XPS (Supplementary Fig. 5), implying the partial oxidation on layered BP, and it provides the possible for BP to connect WO by W-O-P bonds.

The possibility of charge transfer in BP/WO heterostructures were analyzed by the simulations. The density functional theory (DFT) was used to simulate charge interactions between W$_{18}$O$_{49}$ (001) surface and 2D BP to unravel the bonding mechanism. The charge density difference $\Delta \rho = \rho_{W_{18}O_{49}(001)/P} - \rho_{W_{18}O_{49}(001)} - \rho_P$ was calculated as shown in Fig. 2a. Results show that the charge density is redistributed by forming electron-rich and hole-rich regions at interfaces with small amount of P atoms bonded to O atoms. The electrons can be transferred from P to W$_{18}$O$_{49}$ (001) using an O bridge. To confirm our results, the work functions of the W$_{18}$O$_{49}$ (001) surface and black phosphorene were evaluated further. The vacuum levels $E_v$ and Fermi levels $E_f$ were obtained as $E_v(W_{18}O_{49}(001)) = 2.81$ eV, $E_v(P) = 1.25$ eV, $E_f(W_{18}O_{49}(001)) = -2.80$ eV, and $E_f(P) = -3.84$ eV. The work function $W$ can be obtained by $W = E_v - E_f$, further we get $W(W_{18}O_{49}(001)) = 5.61$ eV and $W(P) = 5.09$ eV. The results quantitatively show that electrons can be transferred from BP to W$_{18}$O$_{49}$ (001) surface due to increasing work functions. The electron transfer process was verified by DRS, EPR and XPS spectroscopies, as shown in Figs. 2b-d. Under Vis-NIR irradiation, SPR band of 10-BP/WO becomes stronger with a blue shift as irradiation time prolongs, indicating the increasing electron density on plasmonic WO. The increasing electron density is also observed clearly on EPR spectra of 10-BP/WO after 15 min Vis-NIR irradiation.
While, the DRS (Supplementary Fig. 6) and EPR spectra of plasmonic WO do not have changes under Vis-NIR-irradiation, confirming the electron transfer from BP to WO in BP/WO heterostructures. Moreover, the electron transfer process can also be observed on XPS of W$^{5+}$ 4f (Fig. 2d) which have a pronounced increase on intensity after Vis-NIR irradiation, and the amount of W$^{5+}$ is increased from 19.2 to 34.5 mol% in heterostructures.

The kinetic process of electron transfer in different samples under light irradiation was characterized by using ultrafast transient absorption spectroscopy combined with the femtosecond laser excitation. As shown in transient absorption spectra of BP (Fig. 3a), the electron on VB of BP can be excited in a broad visible spectral region, and the highest photobleaching point is observed at 5.0 ps. Then, the excited electron has a decay resulting in a continuous decrease on spectra as time prolongs. At 2.0 ns, $\Delta A$ is near zero meaning the completed decay of photoelectrons, and BP is recovered from an excited state to the ground state. So, the total lifetime of photoelectron on BP is about 2.0 ns. While, for plasmonic WO, due to the short lifetime of plasmonic carriers$^{48,49}$, the fast decay (< 100 ps) process and weak signals on transient absorption spectra are observed in Fig. 3b. Therefore, the transient absorption spectra (Fig. 3c) of 10-BP/WO heterostructures are mainly from BP, and is much weaker than the spectra of pure BP. The photoelectron decay time (1.0 ns) in 10-BP/WO heterostructure is shorter than that in BP. More detailed photoelectron decay process was studied by the transient absorption kinetic curves (Fig. 3d) collected at $\lambda_{pump} = 675$ nm. Two decay processes of direct decay ($\tau_1$) with short time and trapped state decay ($\tau_2$) with long time are simulated based on the kinetic curve. $\tau_1$ and $\tau_2$ are simulated to be 0.2 ns and 1.8 ns for BP, and 0.16 ns and 1.3 ns for 10-BP/WO. The results indicate that a part of photoelectrons on BP directly transfers to WO, leading to a fast decay process of photoelectrons on BP$^{50}$. Consequently, the photo-excited photoelectrons on BP can transfer to plasmonic WO, and the continuous electron injection can increase the electron density for enhanced SPR.

Photocatalytic performance. The photocatalytic CO$_2$ reduction reaction (CO$_2$-RR) performance is determined in a reactor using a gas-solid configuration. Under Vis-NIR (> 420 nm) light irradiation, 10-BP/WO heterostructures generate 78.3 µmol g$^{-1}$ CO in 3 hours (Fig. 4a), more than 7- and 17-fold higher than 10.9 and 4.4 µmol g$^{-1}$ of plasmonic WO and BP, respectively. CO generation rates (Supplementary Fig. 7) are calculated to be 26.1, 3.6, and 1.5 µmol h$^{-1}$ g$^{-1}$ with a selectivity of 98, 97, and 84 % for 10-BP/WO, WO, and BP, respectively. Meanwhile, a small amount of CH$_4$ is detected for the three samples (Supplementary Fig. 7). Different heterostructures with 2.5, 5.0, 7.5, 10, 12.5, and 15 wt.% BP in composition were synthesized as photocatalysts, and 10-BP/WO exhibited the optimal performance on CO generation (Supplementary Fig. 8). CO generation rates for 2.5-BP/WO, 5.0-BP/WO, 7.5-BP/WO, 10-BP/WO, 12.5-BP/WO, and 15-BP/WO are calculated to 7.3, 9.7, 19.1, 26.1, 20.5, and 11.3 µmol h$^{-1}$ g$^{-1}$ (Fig. 4b), with a selectivity of 91, 95, 95, 98, 98, and 94 %, respectively. With pyroelectric effect and narrow band gap, the increased amount of BP will generate more pyroelectric electrons and photoelectrons to transfer to plasmonic WO which can enhance hot electron generation for CO$_2$-RR. However, as the amount of BP beyond 10 wt%, the plasmonic WO nanowires are covered by BP layers which hinder the
SPR excitation for photocatalytic CO$_2$-RR. CO generated from CO$_2$ is verified by using $^{13}$C-labeled $^{13}$CO for photocatalysis over 10-BP/WO, and $^{13}$CO are detected by the mass spectrometry (MS) as main product (Fig. 4c).

Considering the broad light absorption of 10-BP/WO heterostructures in UV-Vis-NIR region, their photocatalytic performance under different light irradiation was investigated as shown in Fig. 4d. UV- and Vis-irradiation only generates 7.2 and 7.9 µmol g$^{-1}$ CO in 3 hours, respectively. While, NIR-irradiation promotes CO generation to be 12.5 µmol g$^{-1}$ in 3 hours. As Vis-NIR light is irradiated, CO generation is improved to 86.7 µmol g$^{-1}$, 7-fold higher than those under NIR irradiation. While, 109.4 and 148.5 µmol g$^{-1}$ CO is generated under UV-Vis and full-spectrum (UV-Vis-NIR) light irradiation, respectively. CO generation rates (Fig. 4e) are calculated to 2.4, 2.6, 4.2, 36.5, 28.9, and 49.5 µmol g$^{-1}$ h$^{-1}$ CO for UV, Vis, NIR, UV-Vis, Vis-NIR, and UV-Vis-NIR light irradiation, with a selectivity of 95, 94, 99, 100, 98, and 97 %, respectively. Only a little CH$_4$ (< 1 µmol g$^{-1}$ h$^{-1}$) is detected during CO$_2$-RR (Fig. 4e). The stability of 10-BP/WO heterostructures during photocatalytic CO$_2$-RR were investigated as shown in Fig. 4f. Light irradiation containing UV can cause the decreased CO generation over 10-BP/WO, and CO generation rates are reduced from 49.5 to 17.8 and 36.5 to 8.9 µmol g$^{-1}$ h$^{-1}$ for UV-Vis-NIR- and UV-Vis-irradiation, respectively, during three times repeating CO$_2$-RR. The possible reason is the BP decomposition caused by UV-induced oxidation. Fortunately, 10-BP/WO heterostructures have a sustainable performance on CO generation during Vis-NIR-driven CO$_2$-RR. The chemical structure of 10-BP/WO after Vis-NIR-irradiated photocatalysis is analyzed by XPS, and no obvious changes on P 2p and O 1s XPS (Supplementary Figs. 9 and 10) demonstrate their stable structures during CO$_2$-RR. The apparent quantum efficiency (AQE) over different samples during CO$_2$-RR was measured under monochrome light irradiation. AQE of 10-BP/WO (Fig. 4g) has a similar trend with SPR band confirming that photocatalytic CO generation is attributed to SPR excitation. More interesting is that AQE at 900-nm is higher than those in visible region, and it means NIR-irradiation can enhance CO generation. However, AQE (Fig. 6h) of plasmonic WO shows a completely different result, much lower than that of 10-BP/WO in Vis-NIR region. A great difference on AQE indicates that pyroelectric BP can promote CO$_2$-RR for high-selective CO generation. To exclude the influence of photoelectron on BP by Vis-excitation, NIR (> 800) light which can excite SPR of WO but weakly excite BP is used to irradiate BP, WO, 10-BP/WO for CO$_2$-RR (Fig. 4i), and none, 1.1, and 4.2 µmol g$^{-1}$ h$^{-1}$ CO are generated, respectively. NIR-irradiation make SPR excitation to generate hot electrons and thermal energy simultaneously on WO, and the thermal energy can trigger the pyroelectric BP for carriers, facilitating electron transfer from BP to WO and hot electron generation for CO$_2$-RR.

The photothermal effect on 10-BP/WO was further investigated by the thermal camera. Thermal images of 10-BP/WO loaded glass plate (Supplementary Fig. 11) with different Vis-NIR light irradiation time are shown in Fig. 5a. Under Vis-NIR light irradiation, the temperature on 10-BP/WO have a rapidly increase from initial 24.3 °C to 57.1 °C in 2 min, and then to 70.8 °C in 4 min. Finally, the temperature is stabilized at 86 °C after 10 min irradiation. Thermal images and temperatures of 10-BP/WO under different light irradiation are measured in Fig. 5b and Supplementary Figs. 12-16. The temperature is stabilized at 42.5,
62.2, 83, 66.5, 86.3 and 98.5 °C with the ΔT of 15.6, 37.2, 59.7, 40.5, 62.0 and 72.2 °C under 10 min UV, Vis, NIR, UV-Vis, Vis-NIR and UV-Vis-NIR light irradiation, respectively. It is clear that the main contribution on photothermal energy of 10-BP/WO comes from NIR-irradiation, attributing to the strong SPR absorption in NIR region. The photothermal energy generated on plasmonic WO can trigger the pyroelectric BP of heterostructures for carriers and pyroelectric field facilitating the electron transfer to plasmonic WO for CO_2-RR. To verify the contribution of pyroelectric effect on photocatalysis, CO_2-RR under heating (85 °C), Vis-irradiation (420–780 nm) and heating/Vis-irradiation over 10-BP/WO were tested as shown in Fig. 5c, and 1.4, 7.9 and 13.5 µmol g^{-1} CO were obtained in 3 hours, respectively. Only heating on 10-BP/WO do not improve CO_2-RR. However, heating can greatly enhance Vis-driven CO_2-RR on 10-BP/WO. The possible illustration is that the heating triggers the pyroelectric BP to convert thermal energy for carriers and transfer to WO promoting plasmonic CO_2-RR. The influence of heating on CO_2-RR over WO and BP as catalysts were also tested in Fig. 5d, and the heating and Vis-irradiation do not play synergistic roles on CO_2-RR. Consequently, SPR and pyroelectric effect in BP/WO heterostructures play an synergistic role on Vis and NIR light harvesting for continuous electron injection and hot electron generation for high-selective CO generation.

The detailed reaction pathway during CO_2-RR over BP/WO was monitored by in situ FTIR spectra, as shown in Fig. 6a. Before CO_2 absorption in the dark, no remarkable signals are observed on the spectra. After CO_2 saturated absorption for 30 min in the dark, the bands of bidentate carbonate (b-CO_3^{2-}, 1635 cm^{-1}), monodentate carbonate (m-CO_3^{2-}, 1507 cm^{-1}), and bicarbonate (HCO_3^-, 1416 cm^{-1}) are detected on the surface of 10-BP/WO^{51,52}. When Vis-NIR light is irradiated, the intensity of b-CO_3^{2-} bonds has an increase as time prolongs, implying b-CO_3^{2-} as dominant absorption mode on surface. Moreover, the bicarbonate HCO_3^- bands become stronger implying that HCO_3^- is intermediate of CO_2 reduction. So, the possible reaction pathway of CO generation is that CO_2 adsorbed on WO surface forms b-CO_3^{2-}, and then reacts with hot electron and a proton to form intermediate HCO_3^- . HCO_3^- further reacts with electrons and protons to form CO and H_2O. No absorbed *CO is detected by in situ FTIR spectra, indicating the fast desorption of CO as product. The DFT calculations were used to simulate the detailed reaction pathway of CO_2-RR. The Gibbs reaction free energy change (ΔG) during CO_2 reduction over WO_3-x was calculated as shown in Fig. 6b. CO_2 is absorbed on the surface of WO_3-x to be *CO_2 with ΔG = 0.35 eV. Then, one electron and proton are obtained by *CO_2 to be *COOH with ΔG = -0.53 eV. After reaction with the second electron and proton, *COOH becomes *CO with a ΔG = -0.45 eV. *CO reaction for next step has two different pathways, one is to desorb from surface to be free CO with a ΔG = 0.65 eV, and the other one is to reaction with one electron and proton to be *CHO with a ΔG = 0.91 eV which is generally considered as a key step for CH_4 generation. In situ FTIR and DFT simulations demonstrate that CO generation is the main reaction pathway of CO_2-RR over plasmonic WO as photocatalyst, and it is consistent with the experiment results.
Based on above results, the detailed multi-synergetic processes and the possible photocatalytic mechanism are described in schematic diagram (Fig. 6c). With abundant oxygen vacancies, a defect band (DB) formed on the bottom of the conduction band (CB) in WO nanowires. With abundant W$^{5+}$, the DB is occupied by the electrons generating SPR on WO in Vis-NIR region, and the large energy difference between valence band (VB) and lowest unoccupied CB restricts electron excitation from VB to CB under Vis-NIR irradiation. While, the electrons on DB can be excited by SPR to be hot electron in WO. The fast decay process of hot carriers leads to short lifetime of hot electron (< 200 ps) which has been observed on transient absorption spectra (Fig. 4). The nonradiative decay of hot carriers generates photothermal energy causing the low efficiency of plasmonic photocatalysis. Combination of pyroelectric BP and plasmonic WO forms heterostructures, and the plasmonic photothermal energy on WO nanowires can transfer to BP by the thermal radiation, triggering pyroelectric field for carriers on BP. Moreover, the visible irradiation on BP also generates photo-carriers. For plasmonic WO, SPR-excitation can generate hot electrons at high energy levels which are active for photocatalysis. W-O-P bonds connected WO and BP are demonstrated to be channels for electron transfer (ET) from BP to WO. Therefore, the electrons generated by photo-excitation and pyroelectric effects on CB of BP can both transfer to DB of WO with low energy level. The continuous electron injection from BP to plasmonic WO will increase the electron density on DB for stronger SPR which can generate more active hot electrons. Moreover, the continuous electron injection restricts hot electron decay from high energy states to low energy states, promoting hot electrons for CO$_2$ reduction. Meanwhile, the holes left on VB of BP have an oxidization reaction. Under UV-irradiation, electron on VB of WO can be excited to DB of WO leading to the increased electron density for stronger SPR, and it is favor for plasmonic CO$_2$-RR. Meanwhile, the holes left on VB of WO are active to decompose BP, causing the unsustainable activity of heterostructures on photocatalytic CO$_2$-RR. Consequently, multi-physical effects including plasmonic hot carriers and photothermal effect of WO, pyroelectric effect and band excitation of BP, and electron transfer through W-O-P bonds play synergetic roles on enhancing SPR and hot electron generation, boosting high-selective CO$_2$-RR for CO generation.

**Discussion**

In summary, a pyroelectric/plasmonic BP/WO heterostructure was constructed as photocatalysts with multi-physical effects for CO$_2$ reduction. 26.1 µmol h$^{-1}$ g$^{-1}$ CO was generated over the nonmetallic plasmonic heterostructures under Vis-NIR light irradiation with a selectivity of 98%, and which was 7- and 17-fold higher than those of plasmonic WO and BP, respectively. W-O-P bonds connected WO and BP were demonstrated by DFT calculations and verified by various spectroscopic studies as channels for electron transfer from BP to WO. The photothermal energy generated by SPR of WO can make temperature of 10-BP/WO rapidly increase from 24 to 86 °C under Vis-NIR light irradiation, triggering the pyroelectric effect of BP for carriers to promote electron transfer. Therefore, multi-synergistic effects of plasmonic hot carriers and photothermal effect on WO, band excitation and pyroelectric effects on BP, and electron transfer through W-O-P bonds promote hot electron generation for high-selective CO$_2$-RR in Vis-NIR region.
Our work provides clear proofs to demonstrate that constructing multi-physical effects on semiconductors are one promising strategy to improve the Vis-NIR light harvesting for artificial photosynthesis.

**Methods**

**Materials.** Tungsten chloride (WCl$_6$, > 99%) was obtained from Sigma-Aldrich, ethanol (99.8%) was obtained from Macklin chemical reagent Corp, N, N dimethyl formamide (DMF, Aladdin), N-Methyl pyrrolidine (NMP, AR, Aladdin), carbon dioxide (> 99.999%) was obtained Dalian Special Gases Co., LTD, Milli-Q water (18.2 MΩ) was obtained from Sartorius. High-quality of black phosphorus (BP) was purchased from Zhengzhou ADD Intelligent Technology Co., Ltd. (ADDC1911017, www.addtech.net.cn). All the chemical reagents were used as purchased without any further purification.

**Sample preparation.** Layered BP were obtained by using a basic NMP solvent exfoliation method. In detail, 20 mg of bulk BP was first dispersed in 20 mL NMP, and then the dispersion was sonicated for 4 h at 100 W output power under ice-water bath. After exfoliation, the dispersion was centrifuged at 2000 rpm for 20 min with two times to remove non-exfoliated bulk BP. The supernatant was further centrifuged at 11,000 rpm for 20 min to separate BP from the supernatant. After that, the precipitations were re-dispersed in 10 mL NMP with ultrasonic process, resulting in BP NMP dispersion (0.5 mg mL$^{-1}$).

WO$_{3-x}$ (WO) nanowires were obtained by using solvothermal method. In a typical procedure, 150 mg of WCl$_6$ powder was dissolved into 30 mL ethanol, which was vigorously stirred to obtain a yellow suspension. Subsequently, the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave, heated and maintained at 180 °C for 24 h. After naturally cooling down to room temperature, the dark blue powder was separated by centrifugation, washed with ethanol for three times and dried in a vacuum oven for overnight.

BP/WO heterostructures were obtained by a simple ultrasonic process. In brief, BP/NMP solution was centrifuged and washed with ethanol for twice to remove the NMP. Subsequently, the 10 mg WO was dispersed 10 mL ethanol with sonicated for 15 min, then the 2 mL as-prepared BP/ethanol dispersion (0.5 mg mL$^{-1}$) was added into above WO dispersion with sonication for 5 min. Then, the BP/WO were precipitated and obtained by centrifugation. The obtained BP/WO sample was labelled as 10-WO/BP and the different weight ratio BP for WO were prepared by adding different amounts of BP to WO.

**Samples characterization.** The X-ray diffraction (XRD) patterns of the sample were carried out by a Rigaku Rint-2500 diffractometer with Cu K$_\alpha$ radiation at a scanning rate of 0.1° s$^{-1}$. The morphologies were measured by transmission electron microscope (2100, JEOL, operated at 100 kV). X-ray photoelectron spectroscopy (XPS) measurements were performed at a Thermo Fisher Scientific K-ALPHA+ spectrometer. The binding energy was referenced to the C 1s peak at 284.6 eV of the adventitious carbon. Electron paramagnetic resonance (EPR) signal were detected by Bruker A300 spectrometer. UV-Vis-NIR diffuse reflectance spectra (UV-Vis-NIR DRS) were recorded in a UV-Vis/NIR spectrophotometer (JASO V-570). Raman spectra were obtained on a Raman microscopy (XPLORA PLUS, HORIBA) with a
532-nm laser for excitation. Fourier transform infrared (FTIR) spectra were collected by a spectrometer (THERMO) employing KBr disk method. The in situ FTIR spectra were obtained through an in situ diffuse reflectance Fourier transform infrared spectrometer (Nicolet iS50, TMO, US). The sample was degassed for 4 h at 150°C prior to measurement. Then each sample was purged with nitrogen for one hour to blow out all the gases adsorbed on the samples. After that, a mixed gas of CO₂ and water vapor was flowed into the specimen chamber for another hour to ensure sorption equilibrium before irradiation.

**Photocatalytic CO₂ reduction test.** 5 mg sample was mixed with 0.2 mL pure water and plastered on cover glass (4.9 cm⁻²). The cover glass with the sample on the upside was put on the bottom of the reaction chamber (100 mL). The chamber was sealed with thick quartz cover glass and degassed with pure carbon dioxide gas for 20 min. Subsequently, Vis-NIR light supplied by a 300 W xenon lamp (Perfectlight, PLS-SXE300D) equipped with a wavelength cutoff filter (> 400 nm) irradiated the suspension. The gaseous products were analysed by gas chromatography (GC-2014A, Shimadzu) equipped with one TCD and two flame ionization detectors (FID). Other photocatalytic reaction measurements were carried following the above procedure under different light irradiation which is supplied by a 300 W xenon lamp equipped with different-wavelength cutoff filters (< 400nm, 400–780 nm, > 800 nm).

CO₂ photoreduction under monochromatic light using the different monochromatic filters provided the apparent quantum efficiency (AQE). An optical power meter (FZ-A) measured the light intensities. The AQE was calculated based on the following equation: \( \text{AQE} \% = \frac{N \times \text{Number of evolved production molecules}}{\text{Number of incident photons}} \times 100\% \).

**Density functional theory (DFT) calculations.** All density functional theory (DFT) calculations are performed using the Vienna Ab-initio Simulation Package (VASP) software⁵³,⁵⁴ The exchange-correlation functional is approximated by using the generalized gradient approximation (GGA)⁵⁵ with Perdew-Burke-Ernzerhof (PBE)⁵⁶ parametrization. The cutoff energy of the plane-wave is set to be 500 eV to ensure convergence. The convergence criteria of the force and the energy are \( 10^{-3} \) eV/Å and \( 10^{-7} \) eV, respectively. The 2D Brillouin zone integration is done with a k-mesh density of \( 60/a \)⁵⁷ where \( a \) denotes the length of the lattice constant in the unit of Å. In the slab model, the vacuum region is set as 20 Å to avoid interactions between adjacent layers. The \( W_{18}O_{49} \) (001) surface was modeled from the \( W_{18}O_{49} \) bulk unit cell with the optimized lattice parameters of \( a = 3.859 \) Å and \( b = 18.287 \) Å. The black phosphorene was modelled with the optimized lattice parameters of \( a = 4.626 \) Å and \( b = 3.298 \) Å. To simulate the heterostructure \( W_{18}O_{49} \) (001)/ black phosphorene, a supercell \( 4 \times 1 \) of black phosphorene is used to match the \( 1 \times 1 W_{18}O_{49} \) (001) with the optimized lattice parameters of \( a = 4.626 \) Å and \( b = 3.298 \) Å. Due to the absence of strong bonding interactions between \( W_{18}O_{49} \) (001) surface and black phosphorene, the PBE that forms with vdW correction (PBE-D2) is chosen due to the good description of long-range vdW interaction⁵₈.
The free energy computations are performed by using the slab model. A vacuum of approximately 15 Å is placed above the slabs to separate the interaction between periodic images. For $W_{18}O_{49}$ (001) surface slab model, a 1×1 twice atomic layer including 98 S atoms and 36 W atoms is used. The free energy of the adsorbed state is calculated based on the adsorption energy as follows:

$$\Delta G_{\text{ads}} = E_{\text{ads}} + \Delta E_{\text{ZPE}} - T\Delta S,$$

where $E_{\text{ads}}$ is the adsorption energy, and $\Delta E_{\text{ZPE}}$ is the difference corresponding to the zero-point energy between the adsorbed state and the gas phase, $S$ is the entropy, and $T$ is the temperature.

**Declarations**

**Competing interests**

The authors declare no competing interests.

**Additional information**

Supplementary information is available for this paper on the website.

**References**

1. Zhou, L.; Liu, Z. H.; Guan, Z. P.; Tian, B. Z.; Wang, L. Z.; Zhou, Y.; Zhou, Y. B.; Lei, J. Y.; Zhang, J. L.; Liu, Y. D. 0D/2D Plasmonic Cu$_2$ – xS/g-C$_3$N$_4$ Nanosheets Harnessing UV-vis-NIR Broad Spectrum for Photocatalytic Degradation of Antibiotic Pollutant. *Appl. Catal B-Environ.* **263**, 118326 (2020).

2. Liu, Z.; Liu, X. J.; Du, Y. D.; Ren, J. S.; Qu, X. G. Using Plasmonic Copper Sulfide Nanocrystals as Smart Light-Driven Sterilants. *ACS Nano*, **9**, 10335–1034 (2015).

3. Li, J.; Ye, Y. H.; Ye, L. Q.; Su, F. Y.; Ma, Z. Y.; Huang, J. D.; Xie, H. Q.; Doronkin, D. E.; Zimina, A.; Grunwaldt, J. D.; Zhou, Y. Sunlight Induced Photo-Thermal Synergistic Catalytic CO$_2$ Conversion via Localized Surface Plasmon Resonance of MoO$_3$ – x. *J. Mater. Chem. A*, **7**, 2821–2830 (2019).

4. Cheng, H. F.; Qian, X. F.; Kuwahara, Y.; Mori, K.; Yamashita, H. A Plasmonic Molybdenum Oxide Hybrid with Reversible Tunability for Visible-Light-Enhanced Catalytic Reactions. *Adv. Mater.*, **27**, 4616–4621 (2015).

5. Manthiram, K.; Alivisatos, A. P. Tunable Localized Surface Plasmon Resonances in Tungsten Oxide Nanocrystals. *J. Am. Chem. Soc.*, **134**, 3995–3998 (2012).

6. Li, J.; Chen, G. Y.; Yan, J. H.; Huang, B. B.; Cheng, H. F.; Lou, Z. Z.; Li, B. J. Solar-Driven Plasmonic Tungsten Oxides as Catalyst Enhancing Ethanol Dehydration for Highly Selective Ethylene Production. *Appl. Catal. B-Environ.*, **264**, 118517 (2020).

7. Li, Y. X.; Wen, M. M.; Wang, Y.; Tian, G.; Wang, C. Y.; Zhao, J. C. Plasmonic Hot Electrons from Oxygen Vacancies for Infrared Light-Driven Catalytic CO$_2$ Reduction on Bi$_2$O$_3$ – x. *Angew. Chem. Int. Ed.*, **60**, 910–916 (2021).
8. Chen, W.; Li, X. J.; Wang, F.; Javaid, S.; Pang, Y. P.; Chen, J. Y.; Yin, Z. Y.; Wang, S. B.; Li, Y. G.; Jia, G. H. Nonepitaxial Gold-Tipped ZnSe Hybrid Nanorods for Efficient Photocatalytic Hydrogen Production. *Small* **16**, 1902231 (2019).

9. Bian, Z. F.; Tachikawa, T.; Zhang, P.; Fujitsuka, M.; Majima, T. Au/TiO$_2$ Superstructure-Based Plasmonic Photocatalysts Exhibiting Efficient Charge Separation and Unprecedented Activity. *J. Am. Chem. Soc.* **136**, 456–465 (2014).

10. Vu, N. N.; Kaliaguine, S.; Do, T. O. Plasmonic Photocatalysts for Sunlight-Driven Reduction of CO$_2$: Details, Developments, and Perspectives. *ChemSusChem*, **13**, 3967–3991 (2020).

11. Lu, C. H.; Li, J.; Yan, J. H.; Li, B. J.; Huang, B. B.; Lou, Z. Z. Surface Plasmon Resonance and Defects on Tungsten Oxides Synergistically Boost High-Selective CO$_2$ Reduction for Ethylene. *Appl. Mater. Today*, **20**, 100744 (2020).

12. Lu, C. H.; Li, X. R.; Wu, Q.; Li, J.; Wen, L.; Dai, Y.; Huang, B. B.; Li, B. J.; Lou, Z. Z. Constructing Surface Plasmon Resonance on Bi$_2$WO$_6$ to Boost High-Selective CO$_2$ Reduction for Methane. *ACS Nano*, **15**, 3529–3539 (2021).

13. Li, J.; Xu, X. H.; Huang, B. B.; Lou, Z. Z.; Li, B. J. Light-Induced in Situ Formation of a Nonmetallic Plasmonic MoS$_2$/MoO$_3$–$x$ Heterostructure with Efficient Charge Transfer for CO$_2$ Reduction and SERS Detection. *ACS Appl. Mater. Interfaces*, **13**, 10047–10053 (2021).

14. Li, J.; Lou, Z. Z.; Li, B. J. Nanostructured materials with localized surface plasmon resonance for photocatalysis. *Chinese. Chem. Lett.* DOI: 10.1016/j.cclet.2021.07.059 (2021).

15. Yin, H. B.; Kuwahara, Y.; Mori, K.; Yamashita, H. Plasmonic Metal/MoxW$_{1-x}$O$_{3-y}$ for Visible-Light-Enhanced H$_2$ Production from Ammonia Borane. *J. Mater. Chem. A*, **6**, 10932–10938 (2018).

16. Le, H. K. D.; Xiong, H. Y.; Page, B. A.; Garacia-Herrera, L. F.; McAllister, H. P.; Li, B. C.; Wang, H. Y.; Plass, K. E. Effects of I$_2$ on Cu$_{2-x}$S Nanoparticles: Enabling Cation Exchange but Complicating Plasmonics. *ACS Materials Lett.* **2**, 140–146 (2020).

17. Greenberg, B. L.; Ganguly, S.; Held, J. T.; Kramer, N. J.; Mkhoian, K. A.; Aydil, E. S.; Kortshagen, U. R. Nonequilibrium-Plasma-Synthesized ZnO Nanocrystals with Plasmon Resonance Tunable via Al Doping and Quantum Confinement. *Nano Lett.* **15**, 8162–8169 (2015).

18. Zandi, O.; Agrawal, A.; Shearer, A. B.; Reimnitz, L. C.; Dahlman, C. J.; Staller, C. M.; Milliron, D. J. Milliron. Impacts of Surface Depletion on the Plasmonic Properties of Doped Semiconductor Nanocrystals. *Nat. Mater.* **17**, 710–717 (2018).

19. Tandon, B.; Yadav, A.; Khurana, D.; Reddy, P.; Santra, P. K.; Nag, A. Size-Induced Enhancement of Carrier Density, LSPR Quality Factor, and Carrier Mobility in Cr-Sn Doped In$_2$O$_3$ Nanocrystals. *Chem. Mater.* **29**, 9360–9368 (2017).

20. Bhattacharya, C.; Saji, S. E.; Mohan, A.; Madav, V.; Jia, G. H.; Yin, Z. Y. Sustainable Nanoplasmon-Enhanced Photoredox Reactions: Synthesis, Characterization, and Applications. *Adv. Energy Mater.* **10**, 2002402 (2020).
21. Li, J.; Lou, Z. Z.; Li, B. J. Engineering plasmonic semiconductors for enhanced photocatalysis. *J. Mater. Chem. A* DOI: 10.1039/d1ta04541e (2021).

22. Lu, C. H.; Li, J.; Chen, G. Y.; Li, B. J.; Lou, Z. Z. Self-Z-scheme plasmonic tungsten oxide nanowires for boosting ethanol dehydrogenation under UV-visible light irradiation. *Nanoscale* **11**, 12774–12780 (2019).

23. Lou, Z. Z.; Zhang, P.; Li, J.; Yang, X. G.; Huang, B. B.; Li, B. J. Plasmonic Heterostructure TiO$_2$-MCs/WO$_3$-x-NWs with Continuous Photoelectron Injection Boosting Hot Electron for Methane Generation. *Adv. Funct. Mater.* **29**, 1808696 (2019).

24. Liu, Z.; Ren, W. J.; Peng, P.; Guo, S. B.; Lu, T.; Liu, Y.; Dong, X. L.; Wang, G. S. High Performance Bi$_{0.5}$Na$_{0.5}$TiO$_3$-BiAlO$_3$-K$_{0.5}$Na$_{0.5}$NbO$_3$ Lead-Free Pyroelectric Ceramics for Thermal Detectors. *Appl. Phys. Lett.* **112**, 142903 (2018).

25. Suen, J. Y.; Fan, K.; Montoya, J.; Bingham, C.; Stenger, V.; Sriram, S.; Padilla, W. J. Multifunctional Metamaterial Pyroelectric Infrared Detectors. *Optica* **4**, 276–279 (2017).

26. Bowen, C. R.; Taylor, J.; LeBoulbar, E.; Zabek, D.; Chauhanc, A.; Vaish, R. Pyroelectric Materials and Devices for Energy Harvesting Applications. *Energ. Environ. Sci.* **7**, 3836–3856 (2014).

27. Wang, Z.; Yu, R.; Pan, C.; Li, Z. L.; Yang, J.; Yi, F.; Wang, Z. L. Light-Induced Pyroelectric Effect as an Effective Approach for Ultrafast Ultraviolet Nanosensing. *Nat. Commun.* **6**, 8401 (2015).

28. Yang, Y.; Zhou, Y. S.; Wu, J. M.; Wang, Z. L. Single Micro/Nanowire Pyroelectric Nanogenerators as Self-Powered Temperature Sensors. *ACS Nano* **6**, 8456–8461 (2012).

29. Wang, X. F.; Dai, Y. J.; Liu, R. Y.; He, X. Li, S. Wang, Z. L. Light-Triggered Pyroelectric Nanogenerator Based on a pn-Junction for Self-Powered Near-Infrared Photosensing. *ACS Nano* **11**, 8339–8345 (2017).

30. Su, R.; Shen, Y.; Li, L.; Zhang, D.; Yang, G.; Gao, C.; Yang, Y. Silver-Modified Nanosized Ferroelectrics as a Novel Photocatalyst. *Small* **11**, 202–207 (2015).

31. Liu, G.; Ma, L.; Yin, L. C.; Wan, G.; Zhu, H.; Zhen, C.; Yang, Y.; Liang, Y.; Tan, J.; Cheng, H. M. Selective Chemical Epitaxial Growth of TiO$_2$ Islands on Ferroelectric PbTiO$_3$ Crystals to Boost Photocatalytic Activity. *Joule* **2**, 1095–1107 (2018).

32. Li, J.; Cai, L.; Shang, J.; Yu, Y.; Zhang, L. Giant Enhancement of Internal Electric Field Boosting Bulk Charge Separation for Photocatalysis. *Adv. Mater.* **28**, 4059–4064 (2016).

33. Dai, B. Y.; Fang, J. J.; Yu, Y. R.; Sun, M. L.; Huang, H. M.; Lu, C. H.; Kou, J. H.; Zhao, Y. J.; Xu, Z. Z. Construction of Infrared-Light-Responsive Photoinduced Carriers Driver for Enhanced Photocatalytic Hydrogen Evolution. *Adv. Mater.* **32**, 1906361 (2020).

34. You, H. L.; Jia, Y.; Wu, Z.; Wang, F. F.; Huang, H. T.; Wang, Y. Room-Temperature Pyro-Catalytic Hydrogen Generation of 2D Few-Layer Black Phosphorene under Cold-Hot Alternation. *Nat. Comm.* **9**, 2889 (2018).

35. Tian, B.; Tian, B.; Smith, B.; Scott, M. C.; Hua, R.; Lei, Q.; Tian, Y. Supported black phosphorus nanosheets as hydrogen-evolving photocatalyst achieving 5.4% energy conversion efficiency at 353
36. Wu, Z. H.; Lyu, Y.; Zhang, Y.; Ding, R.; Zhang, B.; Yang, Z. B.; Lau, S. P.; Chen, X. H.; Hao, J. H. Large-scale growth of few-layer two-dimensional black phosphorus. *Nat. Mater.* **15**, 6146 (2021).

37. Zhu, X. J.; Zhang, T.; Jiang, D. C.; Duan, H.; Sun, Z.; Zhang, M. M.; Jin, H. C.; Guan, R.; Liu, Y. J.; Chen, M. Q.; Ji, H. X.; Du, P.; Yan, W. S.; Wei, S. Q.; Lu, Y. L.; Yang, S. F. Stabilizing black phosphorus nanosheets via edge-selective bonding of sacrificial C$_{60}$ molecules. *Nat. Commun.* **9**, 4177 (2018).

38. Wang, X. D.; He, J.; Li, J. Y.; Lu, G.; Dong, F.; Majima, T.; Zhu, M. S. Immobilizing Perovskite CsPbBr$_3$ Nanocrystals on Black Phosphorus Nanosheets for Boosting Charge Separation and Photocatalytic CO$_2$ Reduction. *Appl. Catal B-Environ.* **277**, 119230 (2020).

39. Xi, G. C.; Ouyang, S. X.; Li, P.; Ye, J. H.; Ma, Q.; Su, N.; Bai, H.; Wang, C. Ultrathin W$_{18}$O$_{49}$ Nanowires with Diameters below 1 nm: Synthesis, Near-Infrared Absorption, Photoluminescence, and Photochemical Reduction of Carbon Dioxide. *Angew. Chem. Int. Ed.* **51**, 2395–2399 (2012).

40. Hu, J. D.; Chen, D. Y.; Mo, Z.; Li, N. J.; Xu, Q. F.; Li, H.; He, J. H.; Xu, H.; Lu, J. M. Z-Scheme 2D/2D Heterojunction of Black Phosphorus/Monolayer Bi$_2$WO$_6$ Nanosheets with Enhanced Photocatalytic Activities. *Angew. Chem. Int. Ed.* **58**, 2073–2077 (2019).
48. Liu, Z. Q.; Lu, Z. Y.; Bosman, M.; Li, N.; Frankcombe, T. J.; Jia, G. H.; Tricoli, A.; Liu, Y.; Du, Y. P.; Yin, Z. Y. Photoactivity and Stability Co-Enhancement: When Localized Plasmons Meet Oxygen Vacancies in MgO. Small 14, 1803233 (2018).

49. Liu, Y.; Zhang, Z.; Fang, Y.; Liu, B.; Huang, J.; Miao, F.; Bao, Y.; Dong, B. IR-Driven Strong Plasmonic-Coupling on Ag Nanorices/W18O49 Nanowires Heterostructures for Photo/Thermal Synergistic Enhancement of H2 Evolution from Ammonia Borane. Appl. Catal. B Environ. 252, 164–173 (2019).

50. Xu, F. Y; Meng, K.; Cheng, B.; Wang, S. Y.; Xu, J. S.; Yu, J. G. Unique S-scheme heterojunctions in self-assembled TiO2/CsPbBr3 hybrids for CO2 photoreduction. Nat. Commun. 11, 4613 (2020).

51. Liu, L. J.; Jiang, Y. Q.; Zhao, H. L.; Chen, J. T.; Cheng, J. L.; Yang, K. S.; Li, Y. Engineering Coexposed {001} and {101} Facets in Oxygen-Deficient TiO2 Nanocrystals for Enhanced CO2 Photoreduction under Visible Light. ACS Catal. 6, 1097–1108 (2016).

52. Wang, Y.; Arandiyan H.; Scott, J.; Aguey-Zinsou, K. F.; Amal, R. Single Atom and Nanoclustered Pt Catalysts for Selective CO2 Reduction. ACS Appl. Energy Mater. 1, 6781–6789 (2018).

53. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B 54, 11169 (1996).

54. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B 59, 1758 (1999).

55. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 77, 3865 (1996).

56. Perdew, J. P.; Chevry, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. Phys. Rev. B, 46, 6671 (1992).

57. Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. Phys. Rev. B 13, 5188 (1976).

58. Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. J. Comput. Chem. 27, 1787 (2006).

Figures
Figure 1

TEM (a, b), HR-TEM (c), HAADF-STEM (d) and elements mapping images (e-h) of 10-BP/WO heterostructures. P (red), O (green) and W (blue). UV-Vis-NIR diffuse reflectance spectra (DRS, i) and electron paramagnetic resonance (EPR) spectra (j) of WO, BP and 10-BP/WO heterostructures. X-ray photoelectron spectra (XPS) of element P 2p (k) and W 4f (l) on sample BP, WO and 10-BP/WO, respectively.
Figure 2

Top view of charge density difference (a) of black phosphorus/W18O49(001) heterostructure. Blue and yellow isosurfaces represent charge accumulation and depletion in the space with respect to isolated W18O49 (001) surface and black phosphorene. The isovalue is set as 0.53 e/Å³. DRS (b) and EPR spectra (c) of 10-BP/WO heterostructure with different Vis-NIR light irradiation time. W 4f XPS (d) of 10-BP/WO before and after Vis-NIR light irradiation.
Figure 3

Ultrafast transient absorption spectra of BP (a), WO (b) and 10-BP/WO (c), respectively. The corresponding transient absorption kinetic curves (d) on BP and 10-BP/WO collected at $\lambda_{pump}=675$. 
Figure 4

Photocatalytic CO generation (a) over BP, WO and 10-BP/WO heterostructures as catalysts during CO2-RR under Vis-NIR light irradiation. Products generation rates (b) over BP/WO heterostructures with different compositions. Mass spectrometry (MS) spectra (c) of products during CO2-RR by using 13C-isotope labeled 13CO2 as reactants. Photocatalytic CO generation (d) and products generation rates (e) over 10-BP/WO as catalyst different light irradiation: UV (200-420 nm), Vis (420-780 nm), NIR (>780 nm), UV-Vis (200-780 nm), Vis-NIR (>420 nm) and UV-Vis-NIR. CO generation rates (f) over 10-BP/WO during three times recycle CO2-RR under UV-Vis-NIR, UV-Vis and Vis-NIR light irradiation, respectively. Apparent quantum yield (AQE) of 10-BP/WO (g) and WO (h) during photocatalytic CO2-RR. CO generation rates (a) over BP, WO and 10-BP/WO under NIR light (>800 nm) irradiation. Different irradiated light irradiation is supplied by the 300 W xenon lamp equipped with different cut-off filters.
Figure 5

Thermal images (a) of 10-BP/WO heterostructures during photocatalysis under Vis-NIR-irradiation. The temperature changes (b) on 10-BP/WO heterostructures under different light irradiations: UV, Vis, NIR, UV-Vis, Vis-NIR and UV-Vis-NIR light, respectively. CO generation (c, d) over 10-BP/WO, WO and BP as catalysts under heating (85 oC), Vis-irradiation (420-780 nm) and Vis-irradiation/heating, respectively.
Figure 6

In situ FTIR spectra (a) of 10-BP/WO during photocatalytic CO2-RR. The possible reaction pathway (b) of CO2-RR on WO proposed based on the free energy computations by using DFT calculations. Schematic diagram (c) to illustrate the multi-synergetic processes (left) and possible photocatalytic mechanism (right) on plasmonic BP/WO heterostructures. ET (electron transfer), DB (defect band), VB (valence band), CB (conduction band).

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