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 CO₂ for CO under visible-near-infrared (Vis-NIR) light irradiation. Nonmetallic plasmonic heterostructures exhibit 26.1 $\mu\text{mol h}^{-1} \text{g}^{-1}$ 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 CO₂ 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 $10^{18}\text{-}10^{21} \text{ cm}^{-2}$, the surface plasmon resonance (SPR) generally observed on noble metals also occurs on semiconductors such as Cu_{2-x}S ,^{1,2} MoO_{3-x} ,^{3,4} WO_{3-x} ,^{5,6} and $\text{Bi}_2\text{O}_{3-x}$.⁷ Contrast to the metals⁸⁻¹⁰, 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.¹¹⁻¹⁴ Currently, the most reported semiconductors with Vis-NIR SPR absorption are focused on heavily oxygen-vacancy- or cation-vacancy-doped metal oxides^{15,16}, and the heavy doping is a valuable strategy to increase semiconductors' carrier density, resulting in their metalloid properties on optics and catalysis¹⁷⁻²¹. Taking plasmonic WO_{3-x} as an example²²⁻²⁴, 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^{11,22,23}. However, the short lifetime of hot carriers²² 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 catalysis²³⁻³¹. Recently,

a pyroelectric-effect-induced electrical field was used to enhance photo-carriers separation in photocatalyst^{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 photocatalysis³³. Therefore, constructing pyroelectric effect on plasmonic semiconductors will be a new direction for exploring high-efficient photocatalysts. Among various pyroelectric materials, two-dimensional (2D) layered black phosphorus (BP) with broken structure by the loss-of-inversion symmetry exhibits excellent pyroelectric effect and can realize pyro-catalytic H₂ generation under cold-hot alternation³⁴. Owing narrow band gap and pyroelectric effect^[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 structured BP with pyroelectric effect is coupled with plasmonic tungsten oxides (WO₃) to form heterostructures as photocatalysts for CO₂-RR. Under Vis-NIR irradiation, the nonmetallic plasmonic BP/WO heterostructures generate 26.1 $\mu\text{mol h}^{-1} \text{g}^{-1}$ 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_{3-x} (WO) were synthesized by previous reported methods^{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 layers⁴⁰ and {010} facets of W₁₈O₄₉ nanowires⁴¹, 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 $2p_{1/2}$, respectively⁴⁵, and another bond at 133.5 eV is attributed to the oxidized phosphorus (P_xO_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 $W^{6+} 4f_{5/2}$, respectively⁴⁷. 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 $E_{v(W_{18}O_{49}(001))} = 2.81\text{ eV}$, $E_{v(P)} = 1.25\text{ eV}$, $E_{f(W_{18}O_{49}(001))} = -2.80\text{ eV}$, and $E_{f(P)} = -3.84\text{ eV}$. The work function W can be obtained by $W = E_v - E_f$, further we get $W_{W_{18}O_{49}(001)} = 5.61\text{ eV}$ and $W_{(P)} = 5.09\text{ eV}$. 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, ΔA 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 $\lambda_{\text{pump}} = 675 \text{ nm}$. Two decay processes of direct decay (τ_1) with short time and trapped state decay (τ_2) with long time are simulated based on the kinetic curve. τ_1 and τ_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 ($\text{CO}_2\text{-RR}$) performance is determined in a reactor using a gas-solid configuration. Under Vis-NIR (> 420 nm) light irradiation, 10-BP/WO heterostructures generate $78.3 \mu\text{mol g}^{-1} \text{ CO}$ in 3 hours (Fig. 4a), more than 7- and 17-fold higher than 10.9 and $4.4 \mu\text{mol g}^{-1}$ of plasmonic WO and BP, respectively. CO generation rates (Supplementary Fig. 7) are calculated to be 26.1, 3.6, and $1.5 \mu\text{mol h}^{-1} \text{ g}^{-1}$ 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 be 7.3, 9.7, 19.1, 26.1, 20.5, and $11.3 \mu\text{mol h}^{-1} \text{ g}^{-1}$ (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 $\text{CO}_2\text{-RR}$. 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 CO₂-RR. CO generated from CO₂ is verified by using ¹³C-labeled ¹³CO₂ for photocatalysis over 10-BP/WO, and ¹³CO 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 CH₄ (< 1 μmol g⁻¹ h⁻¹) is detected during CO₂-RR (Fig. 4e). The stability of 10-BP/WO heterostructures during photocatalytic CO₂-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 CO₂-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 CO₂-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 CO₂-RR. The apparent quantum efficiency (AQE) over different samples during CO₂-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 CO₂-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 CO₂-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 CO₂-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 CO₂-RR. To verify the contribution of pyroelectric effect on photocatalysis, CO₂-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 $\mu\text{mol g}^{-1}$ CO were obtained in 3 hours, respectively. Only heating on 10-BP/WO do not improve CO₂-RR. However, heating can greatly enhance Vis-driven CO₂-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 CO₂-RR. The influence of heating on CO₂-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 CO₂-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 CO₂-RR over BP/WO was monitored by *in situ* FTIR spectra, as shown in Fig. 6a. Before CO₂ absorption in the dark, no remarkable signals are observed on the spectra. After CO₂ saturated absorption for 30 min in the dark, the bands of bidentate carbonate (b-CO₃²⁻, 1635 cm⁻¹), monodentate carbonate (m-CO₃²⁻, 1507 cm⁻¹), and bicarbonate (HCO₃⁻, 1416 cm⁻¹) are detected on the surface of 10-BP/WO^{51,52}. When Vis-NIR light is irradiated, the intensity of b-CO₃²⁻ bonds has a increase as time prolongs, implying b-CO₃²⁻ as dominant absorption mode on surface. Moreover, the bicarbonate HCO₃⁻ bands become stronger implying that HCO₃⁻ is intermediate of CO₂ reduction. So, the possible reaction pathway of CO generation is that CO₂ adsorbed on WO surface forms b-CO₃²⁻, and then reacts with hot electron and a proton to form intermediate HCO₃⁻. HCO₃⁻ further reacts with electrons and protons to form CO and H₂O. No adsorbed *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 CO₂-RR. The Gibbs reaction free energy change (ΔG) during CO₂ reduction over WO_{3-x} was calculated as shown in Fig. 6b. CO₂ is absorbed on the surface of WO_{3-x} to be *CO₂ with $\Delta G = 0.35$ eV. Then, one electron and proton are obtained by *CO₂ to be *COOH with $\Delta G = -0.53$ eV. After reaction with the second electron and proton, *COOH becomes *CO with a $\Delta G = -0.45$ eV. *CO reaction for next step has two different pathways, one is to desorb from surface to be free CO with a $\Delta G = 0.65$ eV, and the other one is to reaction with one electron and proton to be *CHO with a $\Delta G = 0.91$ eV which is generally considered as a key step for CH₄ generation. *In situ* FTIR and DFT simulations demonstrate that CO generation is the main reaction pathway of CO₂-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 oxidation 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. $26.1 \mu mol h^{-1} g^{-1}$ 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 dioxides (> 99.999%) was obtained Dalian Special Gases Co., LTD, Milli-Q water (18.2 M Ω) 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_α 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: AQE% = (N × Number of evolved production molecules) / (Number of incident photons) × 100%.

Density functional theory (DFT) calculations. All density functional theory (DFT) calculations are performed using the using the Vienna Ab-initio Simulation Package (VASP) software^{53,54} The exchange-correlation functional is approximated by using the generalized gradient approximation (GGA)⁵⁵ with Perdew-Burke-Ernzerhof (PBE)⁵⁶rametrization. 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/a⁵⁷ 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 W₁₈O₄₉ (001) surface was modeled from the W₁₈O₄₉ 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 W₁₈O₄₉ (001)/ black phosphorene, a supercell 4 × 1 of black phosphorene is used to match the 1 × 1 W₁₈O₄₉ (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 W₁₈O₄₉ (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:

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

where E_{ads} is the adsorption energy, and ΔE_{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.

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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 $\lambda_{\text{pump}}=675$.

Figure 4

Photocatalytic CO generation (a) over BP, WO and 10-BP/WO heterostructures as catalysts during CO_2 -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 CO_2 -RR by using ^{13}C -isotope labeled $^{13}\text{CO}_2$ 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 CO_2 -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 CO_2 -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 °C), 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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