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Tridecaboron Diphosphide: A New Infrared Light Active Photocatalyst Efficient CO₂ Photoreduction under Mild Reaction Conditions

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Abstract

The search for efficient infrared (IR) light responsive photocatalysts for photocatalytic CO₂ reduction is highly desirable but remains a huge challenge. Herein, tridecaboron diphosphide (B₁₃P₂) is demonstrated as an effective IR light active photocatalyst for photocatalytic CO₂ reduction reaction. Specifically, B₁₃P₂ exhibits efficient IR light driven photocatalytic CO₂ reduction with a CO evolution rate of 0.13 µmol h⁻¹ and an apparent quantum efficiency (AQE) of 0.07% at the monochromatic light of 810 nm in the presence of Co(bpy)₃²⁺ (bpy = 2'2-bipyridine) as cocatalyst, representing the state-of-the-art IR light active photocatalyst. Both

the theoretical and experimental investigations indicate that $B_{13}P_2$ is a zero bandgap material the online displaying strong light absorption ranging from the ultraviolet to the IR region, and the electron-hole pairs can be generated by the interband transitions between energy orbitals after absorbing photons to participate in the photocatalytic reactions.

Key words: infrared light; tridecaboron diphosphide; novel photocatalyst; photocatalytic CO₂ reduction

1. Introduction

Photocatalysis can directly convert abundant and renewable solar energy into chemical fuels, representing one of the most sustainable and economical strategies to solve the environmental problems and energy crisis.¹ Searching appropriate photocatalytic materials has guided the research of photocatalysis, and numerous semiconductors such as metal sulfides, oxides, phosphides, nitrides and oxynitrides have been demonstrated as effective photocatalysts for various photocatalytic applications.²⁻⁹ Broadening the light absorption range of photocatalysts to infrared (IR) light is a feasible strategy to enhance the photo-conversion efficiency.¹⁰⁻¹² For a semiconductor photocatalyst to absorb more light, its bandgap should be as small as possible.¹³ However, it is very hard for the traditional semiconductor photocatalysts to trigger effective photocatalytic reactions under IR light irradiation, because narrowing the bandgaps of semiconductors via up-shifting the valence band position or down-shifting the conduction band position would inevitably result in the weak driving force for the charge transfer from band edges position to reactants.¹⁴ As such, exploring new photocatalysts via breaking through this limitation on basic principle is highly desirable, with efforts to realize effective IR light driven photocatalysis.

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Up to now, a few unconventional photocatalysts, such as up-conversion materials, view of the online and the onl plasmonic materials have been investigated as IR active photocatalysts.^{15,16} Metallic materials emerge as another type of IR active photocatalysts that have received much attention.^{17,18} Unlike semiconductors, there is almost no energy band gap in metallic materials separating the occupied and unoccupied levels, which endows them the ability to absorb a very wide range of light.¹⁸ Metallic materials can also generate electron-hole pairs via interband transitions after absorbing photons, which can be evidenced by their strong colored features.¹⁸ This indicates that the metallic materials can potentially realize the IR light driven photocatalytic reactions as long as the photogenerated electrons and holes can satisfy the redox potentials of target reactions. On the other hand, another important feature of metallic materials is that they often have much higher carrier density than the conventional semiconductors, which makes them promising application in photocatalysis.¹⁷ Despite the above interesting features, to the best of our knowledge, very few metallic materials were found to possess photocatalytic performances to date, especially for photocatalytic CO₂ reduction under IR light irradiation, largely due to the fact that for most of the metallic materials the redox potential of IR generated electron-hole pairs cannot overcome the activation barriers for photocatalytic CO₂ reduction reaction, and meanwhile the high carrier density in the metallic materials would result in a serious recombination of charges, which inevitably lower the photocatalytic efficiency.^{14,19} Therefore, the search for an appropriate metallic material as an IR active photocatalyst is indispensable while challengeable.

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Tridecaboron diphosphide $(B_{13}P_2)$ is a metal-free compound constructed from boron and phosphorus elements through strong covalent bonding, displaying rhombohedral crystal structure.²⁰ $B_{13}P_2$ possesses excellent chemical stability, which endows it as a promising material for practical applications.²¹ Even though $B_{13}P_2$ has been discovered for decades, to the best of our knowledge, its electronic structure as well as the catalytic properties have never been investigated. In this work, we discover that $B_{13}P_2$ can be applied as a promising photocatalyst

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for photocatalytic CO₂ reduction and H₂ evolution, even under IR light. The stability of Brepeter order in various atmospheres was tested, and the results indicated its highly chemical stability, which was inert to concentrated HNO₃, HCl, H₂SO₄, aqua regia and alkali solution. The valence band X-ray photoelectron spectroscopy (VB-XPS) measurement and theoretical calculations revealed that the B₁₃P₂ possessed continuous electronic occupied states without bandgap. As such, B₁₃P₂ displayed excellent absorption features from the ultraviolet (UV) region to the IR region, and electron-hole pairs could be generated under light irradiation. The photocatalytic performance evaluation indicated that B₁₃P₂ was able to photosplit CO₂ with a CO evolution rate of 0.13 µmol h⁻¹ under IR light and an apparent quantum efficiency (AQE) of 0.07% at the monochromatic light of 810 nm in the presence of Co(bpy)₃²⁺ (bpy = 2'2-bipyridine) as cocatalyst, representing a record high value for IR light driven photocatalytic CO₂ reduction. The photocatalytic CO₂ reduction performances of B₁₃P₂ under full arc and λ >400 nm light could be further promoted, reaching the CO evolution rates of 10.12 µmol h⁻¹ and 1.35 µmol h⁻¹, respectively.

2. Experimental section

2.1 Stability test of tridecaboron diphosphide (B₁₃**P**₂**).** B₁₃**P**₂ was commercially obtained from Mitsuwa Chemicals Co., Ltd (purity >99%). 0.05 g of the B₁₃**P**₂ powder was immersed into 50 ml concentrated HNO₃, concentrated H₂SO₄, concentrated HCl, aqua regia and 5 M NaOH solution, respectively. The above five suspensions were stirred vigorously for 4 hours, and then thoroughly washed with water and collected by centrifugation, and dried for XRD analysis.

2.2 Photocatalytic CO₂ reduction. The photocatalytic CO₂ reduction performance of $B_{13}P_2$ was evaluated in a liquid-solid reaction system at ambient temperature and atmospheric pressure. The experimental setup is shown in Figure S4. Typically, 15 mg of 2'2-bipyridine (bpy) and 1 µmol of CoCl₂ were firstly added into 35 ml of dimethylformamide (DMF) in a 100

ml quartz reactor. After stirring for 5 min, a homogeneous solution was formed. Then 20 marticle Online of B₁₃P₂ photocatalyst and 7 ml of triethanolamine (TEOA) were added in above solution. The reactor was sonicated for a while to obtain well-dispersed solution, and then was connected to the gas-closed system. Before photocatalytic reactions, the system was evacuated for 10 min to remove air, then the system was filled with about 1 bar pure CO₂ gas. A 300 W xenon arc lamp equipped with a UV cutoff filter (λ > 400 nm) or UV-Vis cutoff filter (λ > 780 nm) combined with cooling water filter was applied as the light sources. The produced H₂ and CO were detected and quantified by gas chromatography (GC-8A, Shimadzu Co., Japan) and (GC-14B, Shimadzu Co., Japan), respectively. The isotope-labeled experiment was performed by using ¹³CO₂ as reactant and keeping other reaction conditions unchanged, and the product was investigated by GC-mass spectrum (JEOL-GCQMS, JMS-K9 and 6890N Network GC system, Agilent Technologies). The cycling photocatalytic experiment was conducted as follows. The used B₁₃P₂ photocatalyst was collected by centrifugation followed with washing with DMF for two times, then was re-dispersed in a fresh reaction solution (15 mg of bpy, 1 µmol of CoCl₂, 35 ml of DMF and 7 ml of TEOA) for the next activity test until a total of 6 cycles. The AQE of CO evolution was calculated by the below equation:

AQE (%) = $\frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$

 $\frac{\text{number of evolved CO molecules} \times 2}{\text{number of incident photons}} \times 100\%$

2.3 Photocatalytic H₂ evolution. The photocatalytic H₂ performances were evaluated with 50 mg B₁₃P₂ photocatalyst dispersing in a solution (50 ml H₂O solution containing 20 vol.% methanol as a sacrificial agent, and 2 wt% Pt as cocatalyst) in a 100 ml quartz reactor. The reactor was connected to a glass-closed system, and then was evacuated for 10 min to remove air completely. A 300 W xenon arc lamp with a UV cutoff filter (λ > 400 nm) or UV-Vis cutoff

filter (λ > 780 nm) combined with cooling water filter was applied as the light sources VierMäcle Online produced H₂ was detected and quantified by gas chromatography (GC-8A, Shimadzu Co., Japan).

2.4 Photoelectrochemical measurement. The $B_{13}P_2$ photoelectrode was firstly prepared as follows. 2 mg $B_{13}P_2$ powder was added into 1 ml of ethanol. A well-dispersed solution was obtained after sonication. The 2 mg/ml $B_{13}P_2$ solution was drop by drop uniformly coated onto a ITO substrate surface with an exposed area of $1.0 \times 1.0 \text{ cm}^2$ by spin coating. To improve adhesion, the prepared photoelectrode was further annealed at 300°C in Ar for 2 hours. The linear-sweep-voltammetry (LSV) sweeps were measured in an electrochemical machine (ALS/CH model 650A, Japan) using the $B_{13}P_2$ photoanode as the working electrode, a Ag/AgCl electrode as the reference electrode and a Pt foil as the counter electrode. The electrolyte is 0.5 M Na₂SO₄ solution.

2.5 Characterization. The XRD patterns of the $B_{13}P_2$ were measured by X'Pert PRO diffractometer (PANalytical). The UV-vis-near-IR absorbance spectrum of the $B_{13}P_2$ was obtained on SHIMADZU UV-2600. The SEM image and elemental mapping image of $B_{13}P_2$ powders were obtained on a scanning electron microscope (FE-SEM, JSM-6701F). TEM and HRTEM images of the $B_{13}P_2$ sample were obtained from a transmission electron microscope (TEM, 2100F, JEOL Co., Japan). The chemical states of $B_{13}P_2$ were measured on X-ray photoelectron spectroscopy (XPS, VG-ESCA Mark II).

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2.6 Computational details. The density functional theory (DFT) calculations in this work were performed using the Vienna *Ab initio* Simulation Package (VASP). When doing the calculation, the projector augmented wave (PAW) pseudopotentials were considered, and meanwhile the generalized gradient approximation (GGA) combined with the Perdew-Burke-Ernzerhof (PBE) functional was utilized for the exchange-correlation functional. We expanded the wave-functions by plane-wave and a cutoff energy of 450 eV was used. We set the energy to 10^{-6} eV,

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3. Results and discussion

In this work, commercial $B_{13}P_2$ powder was purchased and used as starting material. The unit cell of B₁₃P₂ is shown in Figure 1a. The B₁₃P₂ has a rhombohedral crystal structure with space group R3m.²⁰ The X-ray diffraction (XRD) pattern of B₁₃P₂ powder reveals its good crystal structure (Figure S1). The BN was confirmed as the impurity in commercial $B_{13}P_2$ powder (Figure S1 and S2). Scanning electron microscopy (SEM) was then employed to investigate the morphology of $B_{13}P_2$. As shown in Figure 1b, $B_{13}P_2$ is a bulk material with particle size ranging from hundreds of nanometers to several micrometers. The elemental mapping images in Figure 1b confirm the uniform distribution of B and P elements. Figure 1c displays the transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of B₁₃P₂. The lattice fringe with a d-spacing of 0.30 nm is observed, which corresponds to the (110) crystal plane distance of $B_{13}P_2$.²⁰ The chemical states of $B_{13}P_2$ were investigated by XPS. As shown in Figure 1d, the B1s spectrum of $B_{13}P_2$ can be successfully fitted to two peaks at 188.2 eV and 191.2 eV, attributed to B-P bond and B-O bond, respectively.^{4,22} The P2p spectrum of B₁₃P₂ can be fitted to a sole peak at 130.4 eV, which is ascribed to B-P bond.⁴ The stability properties of the $B_{13}P_2$ powder were investigated by dispersing the $B_{13}P_2$ powder in concentrated HNO₃, HCl, H₂SO₄, aqua regia and aqueous alkali solution (5 M NaOH) for 4 hours, respectively. It was found that the $B_{13}P_2$ powder was insoluble in aqueous alkali solution or concentrated mineral acids. After acids and aqueous alkali solution treatment, the B₁₃P₂ powder was collected and charaterized by XRD. As shown in Figure S1, the crystal structure of B₁₃P₂ remains almost unchanged after acid and alkali solution treatment, which indicates that B₁₃P₂ exhibits excellent chemical stability and is inert to aqueous alkali solution and concentrated mineral acids.

The optical property of $B_{13}P_2$ was then investigated. $B_{13}P_2$ possesses strong gray color (Figure Colored Co 2a), indicating its intense light absorption ability. According to the UV-vis-near-IR absorbance spectrum in Figure 2a, B₁₃P₂ displays excellent absorption features ranging from the UV to the IR region. In strong contrast to conventional semiconductors, no band edge absorption feature can be observed from $B_{13}P_2$. This is probably due to the fact that $B_{13}P_2$ displays metallic feature rather than semiconducting properties, which can be proved by its VB-XPS spectrum and density functional theory (DFT) calculations. As shown in Figure 2b, the Fermi level (E_f) of $B_{13}P_2$ is occupied by continuous electronic occupied states, revealing its metallic feature. The calculated density of states (DOS) of $B_{13}P_2$ are displayed in Figure 2c, which indicate that the total DOS of $B_{13}P_2$ are mainly attributed to the contribution from the p orbitals of B atom, and the values of DOS around the Fermi level (from -10 eV to 10 eV) are continuous without bandgap, demonstrating the metallic nature of $B_{13}P_2$. The energy band diagram in Figure 2d further reveals the absence of bandgap in $B_{13}P_2$, and the optical absorption of $B_{13}P_2$ from UV to IR probably originates from the electron transfer between each orbital. To reveal whether the charge carriers could be generated over B₁₃P₂ under light irradiation, photoelectrochemical properties were evaluated. Figure S3 shows the linear-sweep-voltammetry (LSV) sweeps for the $B_{13}P_2$ photoanode, which produce apparent photocurrents response to light on-off switching with the bias applied under light irradiation. Even under IR light irradiation, an obvious photocurrent response can also be observed and the generated photocurrent density is even comparable to that from visible light irradiated g-C₃N₄ photoanodes.²³⁻²⁵ These results reveal that B₁₃P₂ is able to produce electron-hole pairs under UV, visible and even IR light irradiation.

Based on the above results, it is interesting to investigate whether the photogenerated electron-hole pairs could participate in photocatalytic reactions. Photocatalytic CO_2 reduction performance was evaluated over $B_{13}P_2$ under IR light. Compared with the intensively investigated systems of UV and visible light driven photocatalytic CO_2 reduction, IR-induced CO_2 reduction to chemical fuels on a photocatalyst has rarely been investigated.^{14,19} This is

mainly due to the fact that a semiconductor photocatalyst that enables photocatalytic VCO ticle Online reduction generally has to possess a large band gap to reach the rather negative CO₂ reduction potential and simultaneously satisfy the requirement of the positive potential for hole consumption (the oxidation of H_2O or sacrificial electron donor), which significantly limits the IR light absorption efficiency.¹⁹ The photocatalytic CO₂ reduction reaction was performed in a dimethylformamide (DMF) solution with triethanolamine (TEOA) and $Co(bpy)_3^{2+}$ as the sacrificial agent and cocatalyst, respectively, under IR light irradiation ($\lambda > 780$ nm, Figure S4), and ambient temperature and pressure. The experimental device is shown in Figure S5. CO and H₂ were generated as the products from this photocatalytic system, while no liquid products evolutions (e.g., HCOOH and CH₃OH) were observed, consistent with results of previous works in a similar liquid-solid reaction system when using TEOA as sacrificial agent and $Co(bpy)_{3^{2+}}$ as cocatalyst.²⁶⁻²⁸ Figure 3a shows the time-dependent CO evolution over $B_{13}P_{2}$ from photocatalytic CO₂ reduction under IR light. It can be seen that the CO yield increases almost lineally with light illumination time, and an evolution rate of 0.13 μ mol h⁻¹ (6.5 μ mol g⁻¹ h⁻¹) is obtained. After 6 hours, 0.78 µmol CO and 0.18 µmol H₂ were generated, referring to the CO selectivity of 81.3%. The achieved IR light driven photocatalytic CO₂ reduction performance over B13P2 is superior to those of the reported IR light active photocatalysts, and is also comparable to those of some UV and visible light responsive photocatalysts, as shown in Table S1.14,19,29-32 To verify the light-responsive activity of B13P2 for CO2 reduction, the wavelength dependent AQE were measured. As shown in Figure 3b, the AQE decreases along with the increasing of light wavelength, demonstrating the CO₂ reduction is driven by the interband transitions related electrons of B₁₃P₂. The longest monochromatic light is chosen at 810 nm due to the instrument limitation. The measured AQE at the monochromatic light of 810 nm over B₁₃P₂ reaches up to 0.07%, representing a record high value for IR light driven photocatalytic CO₂ reduction.⁵ Under IR light irradiation, the temperature in the reaction solution is measured at around 25 °C. In a controlled experiment performed under 25 °C without

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light irradiation, no CO product is detected, which excludes the thermal effect for the VCO product contine reduction performance (Figure S6). We further tested the effects of the reaction solvent on the photocatalytic CO₂ reduction performance of $B_{13}P_2$ (Figure S7). It shows that both the DMF and acetonitrile solvents are favorable for the photocatalytic CO₂ reduction reaction mainly because of their excellent solubility of CO₂ molecular.³³ However, the photocatalytic CO₂ reduction reaction performance greatly decreases when water is used as solvent, largely ascribed to the weak chemical affinity of water towards CO₂ molecules.³³

The stability of $B_{13}P_2$ photocatalyst was then examined by repeatedly conducting the photocatalytic CO₂ reduction reactions under IR light. As shown in Figure 3a, no obvious deactivation of CO evolution rate is found during 6 cycles tests. Moreover, XRD characterization of the used B₁₃P₂ after photocatalytic reaction also proves its high stability feature (Figure S8). Figure 3c shows the photocatalytic CO₂ reduction activities under different conditions. The evolution of CO is greatly suppressed without $Co(bpy)_3^{2+}$, indicating the significant role of Co(bpy)₃²⁺ as cocatalyst for promoting photocatalytic CO₂ reduction (Figure 3c, column 2). No products are detected in the dark or in the absence of $B_{13}P_2$, suggesting CO is produced through a photocatalytic pathway over $B_{13}P_2$ photocatalyst (Figure 3c, column 4, 5). When TEOA is removed from the photocatalytic system under otherwise identical conditions, no products are generated, indicating TEOA is both the proton source and electron donor in the photocatalytic CO₂ reduction reaction (Figure 3c, column 6), since the CO and H₂ evolutions are proton and electron involved reactions ($CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$; $2H^+$ + $2e^- \longrightarrow H_2$). Only H₂ is produced under Ar, indicating the produced CO originates from CO_2 (Figure 3c, column 3). In order to directly reveal the carbon source of the produced CO, isotopic experiment was conducted in the presence of ¹³CO₂. The gas chromatogram (GC) and mass spectra (MS) were used to analyze the generated gas products. As shown in Figure 3d, a peak at the retention time of 6.1 min in GC spectrum refers to the CO product, and other two peaks before CO are demonstrated to be the O_2 and N_2 in the sampling needle. The m/z= 29 in

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MS is observed by analyzing the CO product, which is ascribed to the ¹³CO. This result directly intervent of the directly intervent of the source of CO originates from CO₂. The photocatalytic performances were further evaluated under full arc (UV+ Vis + IR) and λ >400 nm (Vis+ IR) light irradiation. As shown in Figure 4, the photocatalytic CO₂ reduction performances under full arc and λ >400 nm light are dramatically improved compared with that under IR light, reaching the CO evolution rates of 10.12 µmol h⁻¹ and 1.35 µmol h⁻¹, respectively. Only trace amount of CO and H₂ can be detected when using BN as catalyst, which demonstrates that the high yield of CO and H₂ under full arc originates from the photoexcitation of B₁₃P₂ (Figure S9). Not only limited to the photocatalytic CO₂ reaction, B₁₃P₂ also exhibits photocatalytic H₂ evolution performance in water using methanol as a sacrificial agent and in-situ photo-deposited Pt as cocatalyst under visible light and IR light. As shown in Figure S10, steady H₂ evolution is observed over B₁₃P₂ in photocatalysis.

To understand the mechanism of $B_{13}P_2$ in photocatalysis, the work function value (φ) of $B_{13}P_2$ was calculated using first-principle methods, and the bulk model of $B_{13}P_2$ crystal with the surface of (110) was selected on the basis of the XRD and the HR-TEM micrographs results. As shown in Figure 5a, the work function value (φ) of $B_{13}P_2$ is calculated to be 4.98 eV. In other words, the Fermi level (E_f) can be estimated as 4.98 eV relative to the vacuum level. The E_f value is then converted to electrochemical energy potential on the basis of the reference standard that 0 V versus RHE (reversible hydrogen electrode) corresponds to -4.44 eV versus evac (vacuum level), which is +0.54 V vs. RHE.³⁴ Charge density distribution of $B_{13}P_2$ is shown in Figure 5b, which shows that there exists the charge transfer from P to B site through the B-P bonding in $B_{13}P_2$ could be then transferred to cocatalytic materials (Pt or Co(bpy)₃²⁺) under light irradiation. Previous studies have revealed that Co (I) generated by in-situ photoreduction of Co (II) bipyridine is the active site for photocatalytic CO₂ reduction reaction, and the redox

potential of Co (II)/Co (I) locates at around -0.44 V vs NHE.³⁵ The energy difference betweetice Online the E_f value and the redox potential of Co (II)/Co (I) is 0.92 V, which indicates that the IR light irradiation on B₁₃P₂ is theoretically possible to reduce Co (II), as the photonic energy of IR light can reach 1.55 eV.⁵ To give the direct evidence of the generation of Co (I), electron spin resonance (ESR) measurement was performed. As shown in Figure S11, under IR light irradiation, the ESR signal is weakened, indicating the high-spin-state Co (II) is reduced to lowspin-state Co (I).³⁶ The proposed photocatalytic CO_2 reduction process over $B_{13}P_2$ is shown in Figure 5c and Figure S12. Under light irradiation, electron-hole pairs are generated over $B_{13}P_2$ through interband transition between different orbitals, and electrons will leap over the Fermi level to a higher energy level. The electrons with energy level above the redox potential of Co (II)/Co (I) can be injected into $Co(bpy)_3^{2+}$ to produce Co (I), which is responsible for the CO_2 reduction.

4. Conclusion

In summary, this study provides strong evidence for the potential application of $B_{13}P_2$ as a novel IR active photocatalyst in photocatalytic CO₂ reduction. The photocatalytic performance evaluation shows that B₁₃P₂ is able to stably photosplit CO₂ under IR light with a CO evolution rate of 0.13 μ mol h⁻¹ in the presence of Co(bpy)₃²⁺ as cocatalyst, and the measured AQE at the monochromatic light of 810 nm reaches up to 0.07%, representing a record high value for IR light driven photocatalytic CO2 reduction. The photocatalytic CO2 reduction performances of $B_{13}P_2$ under full arc and λ >400 nm light can be further promoted, reaching the CO evolution rates of 10.12 µmol h⁻¹ and 1.35 µmol h⁻¹, respectively. Not only limited to the photocatalytic CO₂ reaction, B₁₃P₂ also exhibits photocatalytic H₂ evolution performance in water under both visible light and IR light. Both the theoretical and experimental evidences indicate the zero bandgap feature of B₁₃P₂, which displays intensive and broad light absorption ranging from the UV to the IR region, and electron-hole pairs are generated in $B_{13}P_2$ by the interband transitions

between energy orbitals after absorbing photons to participate in the photocatalytic reactionstice online $B_{13}P_2$ shows highly chemical stability, inert to concentrated HNO₃, HCl, H₂SO₄, aqua regia and alkali solution, which endows it as a promising material for practical applications. It is expected that $B_{13}P_2$ will provide new opportunities for the development of IR responsive photocatalysts, photodetectors, solar cells and many other solar energy conversion systems.

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Declaration of interests

The authors declare no competing financial interests.

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Figure 1. (a) Unit cell of $B_{13}P_2$. (b) SEM image of $B_{13}P_2$ and the corresponding elemental mapping images of B and P. (c) TEM and HRTEM images of $B_{13}P_2$. (d) B 1s and P 2p XPS spectra of $B_{13}P_2$.

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Figure 2. (a) UV-vis-near-IR absorbance spectrum and photograph of $B_{13}P_2$. (b) VB-XPS spectrum of $B_{13}P_2$. (c) Calculated DOS and (d) energy band diagram of $B_{13}P_2$.



Figure 3. (a) CO evolution as a function of reaction time under IR light over $B_{13}P_2$. (b) AQE as a function of incident light wavelength over $B_{13}P_2$. (c) CO and H_2 evolution amount in 6 hours under various reaction conditions. (d) GC-MS spectra of CO obtained from ¹³CO₂ isotope experiment over $B_{13}P_2$ under IR light.

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Figure 4. (a) CO evolution from photocatalytic CO₂ reduction over $B_{13}P_2$ in the presence of $Co(bpy)_3^{2+}$ as cocatalyst under full arc and λ >400 nm (Vis+ IR) light irradiation in DMF/TEOA solution. (b) Comparison of photocatalytic CO₂ reduction performances under full arc and λ >400 nm (Vis+ IR) light after 6 hours reaction.



Figure 5. (a) Work function calculation for $B_{13}P_2(110)$. (b) Charge density distributions of $B_{13}P_2$, and the value of isosurface is 0.01 e/A3. Green ball and purple ball refer to B and P, respectively. (c) The mechanism of photocatalytic CO₂ reduction over $B_{13}P_2$ in the presence of Co(bpy)₃²⁺ as cocatalyst.

TOC figure

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Tridecaboron diphosphide $(B_{13}P_2)$ is demonstrated as a novel and effective IR light active photocatalyst for photocatalytic CO₂ reduction reaction. $B_{13}P_2$ displays intensive and broad light absorption ability, and the electron-hole pairs generated by the interband transitions between energy orbitals can participate in the photocatalytic reactions.