

Synthesis and photocatalytic CO₂ reduction performance of metalloporphyrin and H₅[PMo₁₀V₂O₄₀]·34.5H₂O composite catalyst

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Inspired by the structural motifs of chlorophyll, a series of bio-inspired Z-scheme heterojunction photocatalysts yPMo₁₀V₂/CoTPyP were constructed by integrating metalloporphyrin CoTPyP with H₅[PMo₁₀V₂O₄₀]·34.5H₂O. The optimized 0.1PMo₁₀V₂/CoTPyP heterojunction exhibits remarkable photocatalytic CO₂ reduction performance, achieving a CO production rate of 316.88 μmol·g⁻¹·h⁻¹, which is 3.7 times and 5.9 times higher than those of CoTPyP and H₂TPyP, respectively. Systematic characterization confirms that the Z-scheme electron transfer mechanism effectively promotes charge separation while maintaining high redox capability. This work demonstrates the feasibility of mimicking natural photosynthesis through rational material design and provides valuable insights for developing efficient artificial photosynthetic systems.

metalloporphyrin; polymetaloxoanions; photocatalytic CO₂ reduction; Z-scheme

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1. Introduction

Converting CO₂ into valuable fuels and chemicals using solar energy is a promising strategy to combat climate change and enable sustainable development^[1]. Nevertheless, the high stability of the linear CO₂ molecule poses a fundamental challenge for its activation under mild conditions^[2]. Traditional photocatalysts including semiconductors (e.g., TiO₂, CdS) and metal-organic frameworks typically suffer from limited light absorption, rapid carrier recombination, and inadequate cycling stability^[3-5]. By mimicking the light-reaction steps of natural photosynthesis, the construction of bio-inspired Z-scheme heterojunction photocatalysts not only broadens the spectral response but also effectively promotes the separation and utilization of photogenerated electron-hole pairs^[6-8].

Porphyrin-based compounds possess a large specific surface area, tunable molecular structures, and remarkable photostability^[9-10]. A key advantage lies in their strong ab-

sorption across the visible spectrum, characterized by distinct Soret (400 to 450 nm) and Q (500 to 650 nm) bands^[11]. Furthermore, the nitrogen atoms within the porphyrin ring enable coordination with metal ions, forming metal porphyrins that structurally resemble natural chlorophyll^[12]. Owing to their superior photophysical and catalytic properties, metal porphyrins are extensively employed as active centers in photocatalytic CO₂ reduction^[13]. Guo et al.^[14] developed a bimetallic Z-scheme heterojunction (CoPor-RuN₃) based on cobalt porphyrin and ruthenium complex, which showed outstanding CO₂ photoreduction performance. This high activity stems from the synergy between Co and Ru dual sites and the Z-scheme facilitated charge separation.

Polyoxometalates (POMs) have shown remarkable potential in photocatalytic CO₂ reduction due to their excellent redox properties and multi-electron storage/release capabilities^[15-16]. However, most POMs act as homogeneous catalysts in these reactions, hindering their recovery and reuse and creating potential environmental issues^[17]. By integrating POMs with semiconductor photocatalysts to form bio-inspired Z-scheme heterojunctions, it is possible to retain their advantageous properties while overcoming the challenges related to catalyst recovery^[18]. Moreover, the

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high solubility of POMs facilitates the formation of well-defined heterointerfaces^[19]. These characteristics make POMs promising candidates to replace photosystem II (PS II) in artificial Z-scheme photocatalytic systems.

Porphyrin H₂TPyP and the transition metal-incorporated metalloporphyrins TMTPyP (TM = Fe, Co, Ni), structurally analogous to chlorophyll, were synthesized in this work. Through supramolecular self-assembly, CoTPyP, which exhibited the highest photocatalytic activity, was combined with H₅[PMo₁₀V₂O₄₀]·34.5H₂O (abbreviated as PMo₁₀V₂) to fabricate a series of bio-inspired Z-scheme heterojunction photocatalysts designated as *y*PMo₁₀V₂/CoTPyP (*y* = 1.0, 0.5, 0.2, 0.1, and 0.05, where *y* represents the mass ratio of PMo₁₀V₂ to CoTPyP). Results demonstrated that the formation of heterojunctions enhanced the photocatalytic performance. Specifically, 0.1PMo₁₀V₂/CoTPyP exhibited a CO production rate of 316.88 μmol·g⁻¹·h⁻¹ in photocatalytic CO₂ reduction, representing 3.7-fold and 5.9-fold improvements over CoTPyP and H₂TPyP, respectively. Furthermore, the electron transfer mechanism of the Z-scheme heterojunction was elucidated. This study provides important guidance for constructing efficient bio-inspired Z-scheme heterojunction photocatalysts that mimic the electron transfer mechanism in natural photosynthesis.

2. Results and discussion

2.1 Morphological and structural characterization

The morphology of the synthesized samples was characterized by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Figure S1 shows the SEM images of H₂TPyP and TMTPyP (TM = Fe, Co, Ni). The SEM results indicate that the H₂TPyP exhibits a bulk stacked morphology, whereas the incorporation of transition metals leads to noticeable morphological changes, suggesting that metal doping plays a role in modulating the structure of material. In particular, CoTPyP displays a thin layered sheet-like structure, which is beneficial for photocatalytic CO₂ reduction. This layered architecture helps to increase the specific surface area of the photocatalyst, thereby providing more active sites for the adsorption and activation of CO₂ molecules. This finding

was corroborated by N₂ adsorption-desorption analysis. As shown in Figure S2, H₂TPyP, CoTPyP, and 0.1PMo₁₀V₂/CoTPyP exhibit distinct N₂ adsorption-desorption isotherms. The Brunauer-Emmett-Teller (BET) surface areas were calculated to be 4, 39, and 434 m²·g⁻¹ for H₂TPyP, CoTPyP, and 0.1PMo₁₀V₂/CoTPyP, respectively. The introduction of transition metal ions induced a morphological evolution from multilayered bulk stacking in H₂TPyP to thin sheet-like structures in CoTPyP, resulting in an approximately tenfold increase in surface area. Moreover, the absence of metal oxide nanoparticles in the SEM images confirms that the metal species were successfully incorporated into the porphyrin framework in ionic form rather than as separate phases.

Upon the formation of the 0.1PMo₁₀V₂/CoTPyP heterojunction *via* supramolecular self-assembly between CoTPyP and PMo₁₀V₂, no significant morphological change was observed. The composite retained a thin sheet-like structure similar to that of pristine CoTPyP (See Figure 1a), indicating that the introduction of PMo₁₀V₂ and the construction of the heterojunction did not alter the fundamental framework of the metalloporphyrin. The layered morphology was further confirmed by the HRTEM image of 0.1PMo₁₀V₂/CoTPyP (See Figure 1b). Moreover, the TEM image and corresponding elemental mapping (See Figure S3) revealed the co-existence and uniform distribution of Co, C, N, O, P, Mo, and V throughout the structure. These results confirm the successful incorporation of cobalt into the H₂TPyP skeleton and the homogeneous dispersion of PMo₁₀V₂ on the CoTPyP nanosheets.

The structure of the synthesized heterojunction photocatalyst was characterized by X-ray powder diffraction (XRD). As shown in Figure 2a, H₂TPyP is identified to be a triclinic crystal with the space group *P*₁^[20]. Compared with H₂TPyP, the XRD patterns of metal-incorporated TMTPyP (TM = Fe, Co, Ni) show no significant shift in diffraction peak positions, but a noticeable reduction in intensity. This decrease may be attributed to the incorporation of transition metals into the porphyrin skeleton *via* the formation of TM-N_x coordination bonds, which likely suppresses the thermal polycondensation of H₂TPyP^[21]. According to previous literature, the XRD peaks observed at 8° to 10°, 18° to 22°, and 24° to 30° can be assigned to the characteristic Keggin-

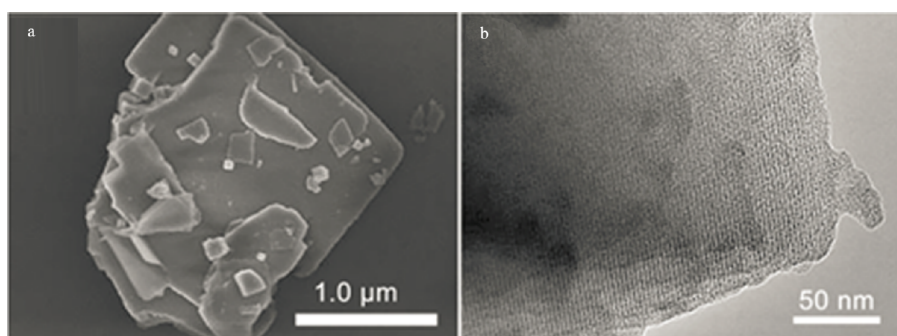


Figure 1 SEM (a) and HRTEM image (b) of 0.1PMo₁₀V₂/CoTPyP

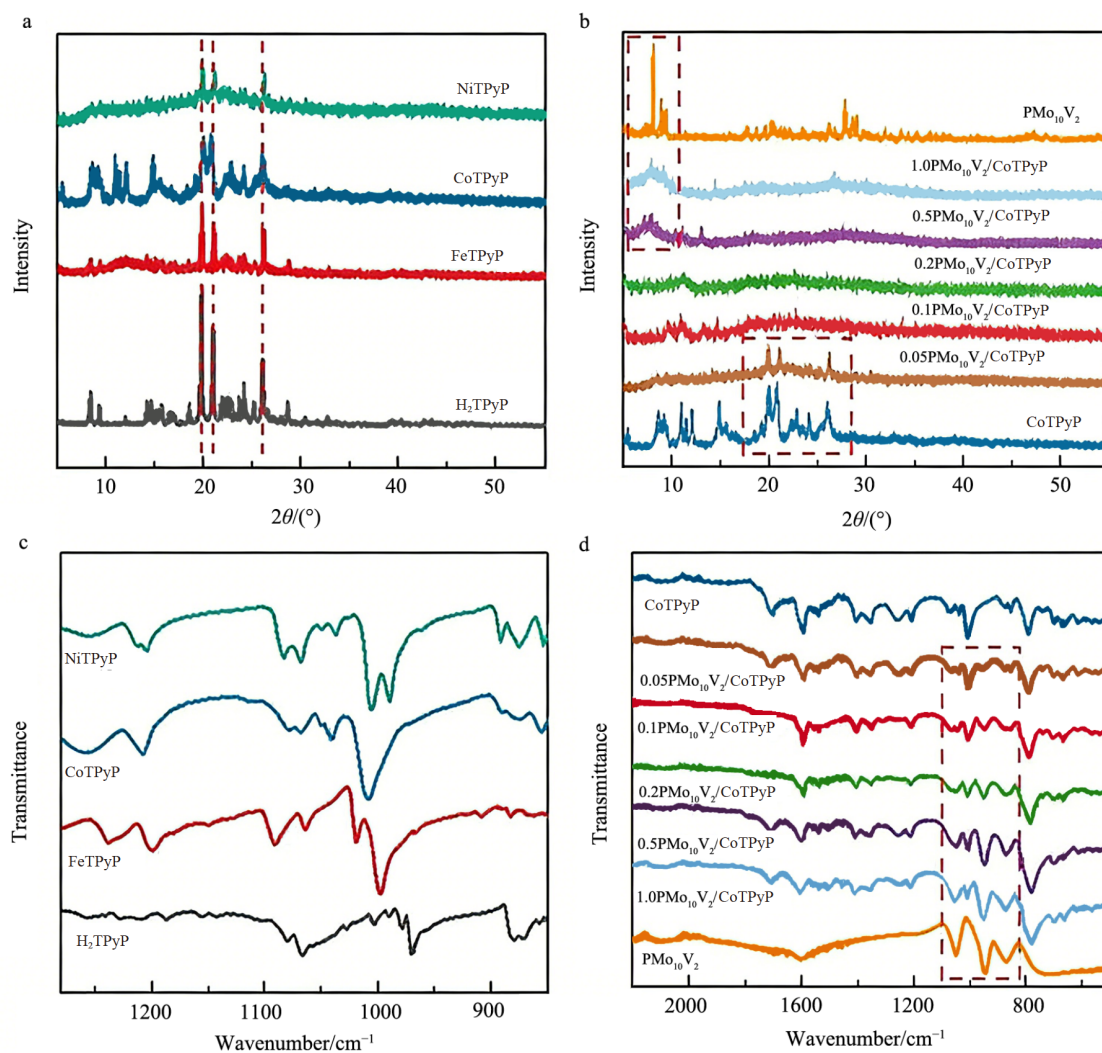


Figure 2 XRD patterns (a and b) and FT-IR spectra (c and d) of H_2TPyP , TMTPyP, $yPMo_{10}V_2/CoTPyP$ and $PMo_{10}V_2$

type $PMo_{10}V_2$ structure^[22]. In the XRD patterns of $yPMo_{10}V_2/CoTPyP$ composites (See Figure 2b), with increasing $PMo_{10}V_2$ content, the diffraction peak intensities of polycrystalline CoTPyP gradually weaken, while those corresponding to the Keggin structure of $PMo_{10}V_2$ intensify. These results provide evidence for the successful formation of $PMo_{10}V_2/CoTPyP$ composites.

The structure of the synthesized heterojunction photocatalysts was further investigated by Fourier transform infrared (FT-IR) spectroscopy. As shown in Figure 2c, H_2TPyP exhibits a weak bending vibration peak of N—H at 976 cm^{-1} . After metal coordination, this peak disappears and a new stretching vibration assigned to the TM— N_x bond emerges near 1000 cm^{-1} , confirming the successful formation of a metal-porphyrin coordination structure^[23]. Moreover, the FT-IR spectra of TMTPyP show no significant changes compared to that of H_2TPyP , indicating that the incorporation of transition metals does not alter the fundamental skeleton of the porphyrin. In the FT-IR spectra of $yPMo_{10}V_2/CoTPyP$ composites (See Figure 2d), characteristic peaks of both CoTPyP and the Keggin-structured $PMo_{10}V_2$ are present. With decreasing content of $PMo_{10}V_2$,

the intensity of the characteristic peaks associated with the Keggin structure gradually weakens, providing additional evidence for the successful synthesis of the $yPMo_{10}V_2/CoTPyP$ heterojunction photocatalysts. X-ray photoelectron spectroscopy (XPS) was employed to investigate the elemental composition and surface chemical states of samples. The XPS survey spectrum of $0.1PMo_{10}V_2/CoTPyP$ (See Figure S3) reveals the presence of Co, C, N, and O originating from the porphyrin structure, along with characteristic peaks of Mo, confirming the successful incorporation of $PMo_{10}V_2$ in the heterojunction photocatalyst. However, no characteristic signals of P or V were detected, which can be attributed to the low loading amount and homogeneous dispersion of $PMo_{10}V_2$.

The high-resolution C-1s spectrum of CoTPyP (See Figure 3a) displays two distinct peaks. The peak at 284.6 eV is assigned to sp^2 -hybridized C—C bonds in the porphyrin skeleton, while the signal at 285.6 eV corresponds to C—N bonds. The N-1s spectrum (See Figure 3b) exhibits three characteristic peaks at 398.6 , 399.2 , and 400.3 eV , which are attributed to pyridinic nitrogen, metal-coordinated TM— N_x bonds, and pyrrolic nitrogen in the porphyrin ring, respec-

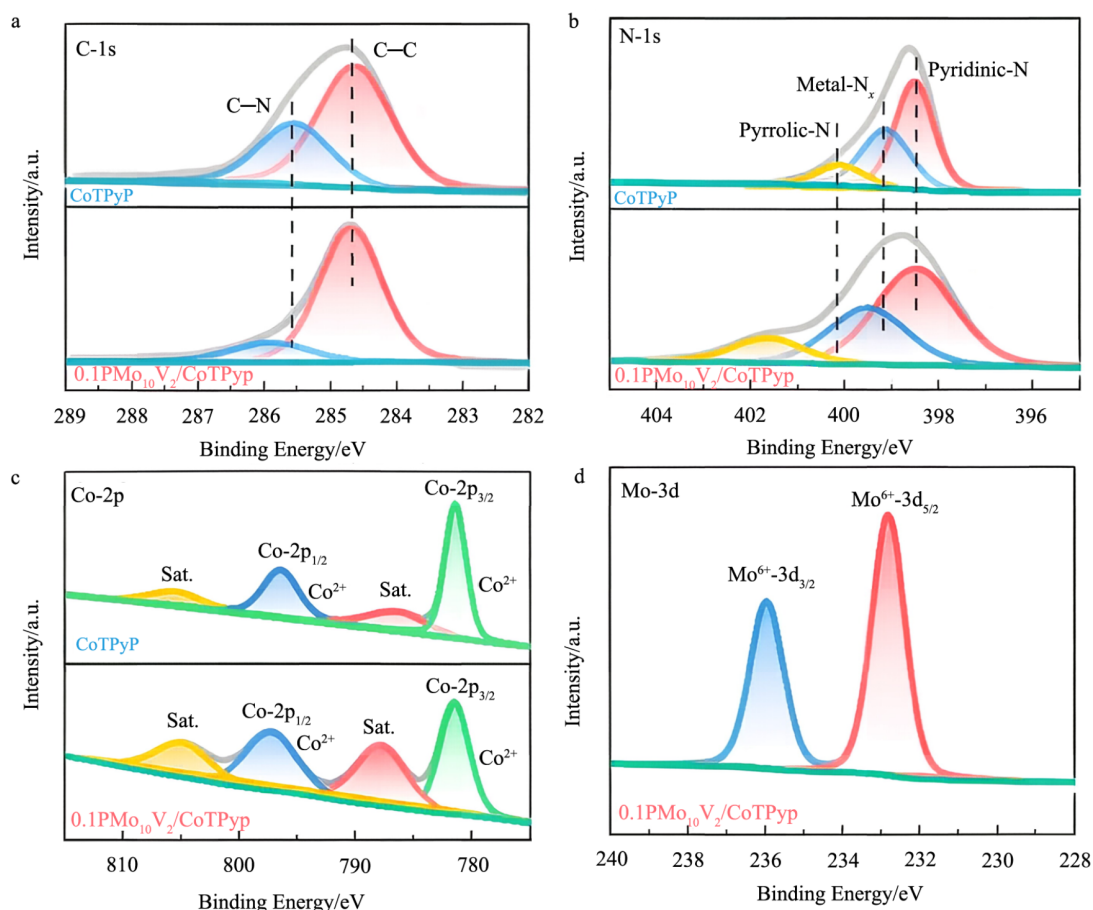


Figure 3 High-resolution XPS spectra of CoTPyP and 0.1PMo₁₀V₂/CoTPyP

tively. The high-resolution Co-2p spectrum (See Figure 3c) exhibits two characteristic peaks of Co²⁺. The peaks located at 780.2 and 797.2 eV correspond to Co²⁺-2p_{3/2} and Co²⁺-2p_{1/2}, respectively, confirming the successful incorporation of Co²⁺ into the porphyrin skeleton *via* coordination with nitrogen atoms in the porphyrin ring. In the Mo-3d spectrum (See Figure 3d), two peaks are observed at 232.8 and 236.0 eV, corresponding to Mo⁶⁺-3d_{5/2} and Mo⁶⁺-3d_{3/2}, respectively. In the XPS spectra of 0.1PMo₁₀V₂/CoTPyP, the characteristic peaks of both C-1s and N-1s shift toward higher binding energies. This positive shift can be attributed to electron transfer from CoTPyP to PMo₁₀V₂, accompanied by electrostatic interactions between protonated CoTPyP and the negatively charged PMo₁₀V₂.

2.2 Optical properties

To further investigate the optical properties of the photocatalysts, UV-visible diffuse reflectance spectroscopy was performed. As shown in Figure 4a, all samples exhibit characteristic absorption bands of porphyrin, with an intense Soret (B) band at 380 to 470 nm and moderately strong Q bands in the 500 to 680 nm region. Upon the introduction of POMs, the absorption of samples increased significantly. Moreover, this enhancement was dependent on the PMo₁₀V₂ loading content. The band gaps (E_g) of CoTPyP and

PMo₁₀V₂ were calculated to be 2.37 and 1.97 eV, respectively by the Kubelka-Munk function (See Figure 4b). To determine the conduction band (CB) positions of CoTPyP and the frontier molecular orbital energy levels of PMo₁₀V₂, the Mott-Schottky (MS) and cyclic voltammetry (CV) were carried out. As shown in Figure 4c, the positive slope of the Mott-Schottky plot indicates that CoTPyP is an N-type semiconductor with a CB of −0.80 eV (*vs.* NHE). The cyclic voltammetry curve reveals a LUMO (lowest unoccupied molecular orbital) level of 0.82 eV (*vs.* NHE) for PMo₁₀V₂. Based on these data, the valence band (VB) potential of CoTPyP and the HOMO (highest occupied molecular orbital) level of PMo₁₀V₂ were calculated to be 1.57 and 2.79 eV (*vs.* NHE). Based on the above, the energy level diagrams of CoTPyP and PMo₁₀V₂ were constructed, as illustrated in Figure 4d. Owing to the close alignment between the VB of CoTPyP and the LUMO of PMo₁₀V₂, and considering that the conduction band potential of CoTPyP is higher than the redox potential for photocatalytic CO₂ reduction to CO (−0.53 V *vs.* NHE), the yPMo₁₀V₂/CoTPyP composite is capable of driving photocatalytic CO₂ reduction *via* a Z-scheme electron transfer pathway.

2.3 Photoelectrochemical measurements

Figure 5a shows the transient photocurrent responses of

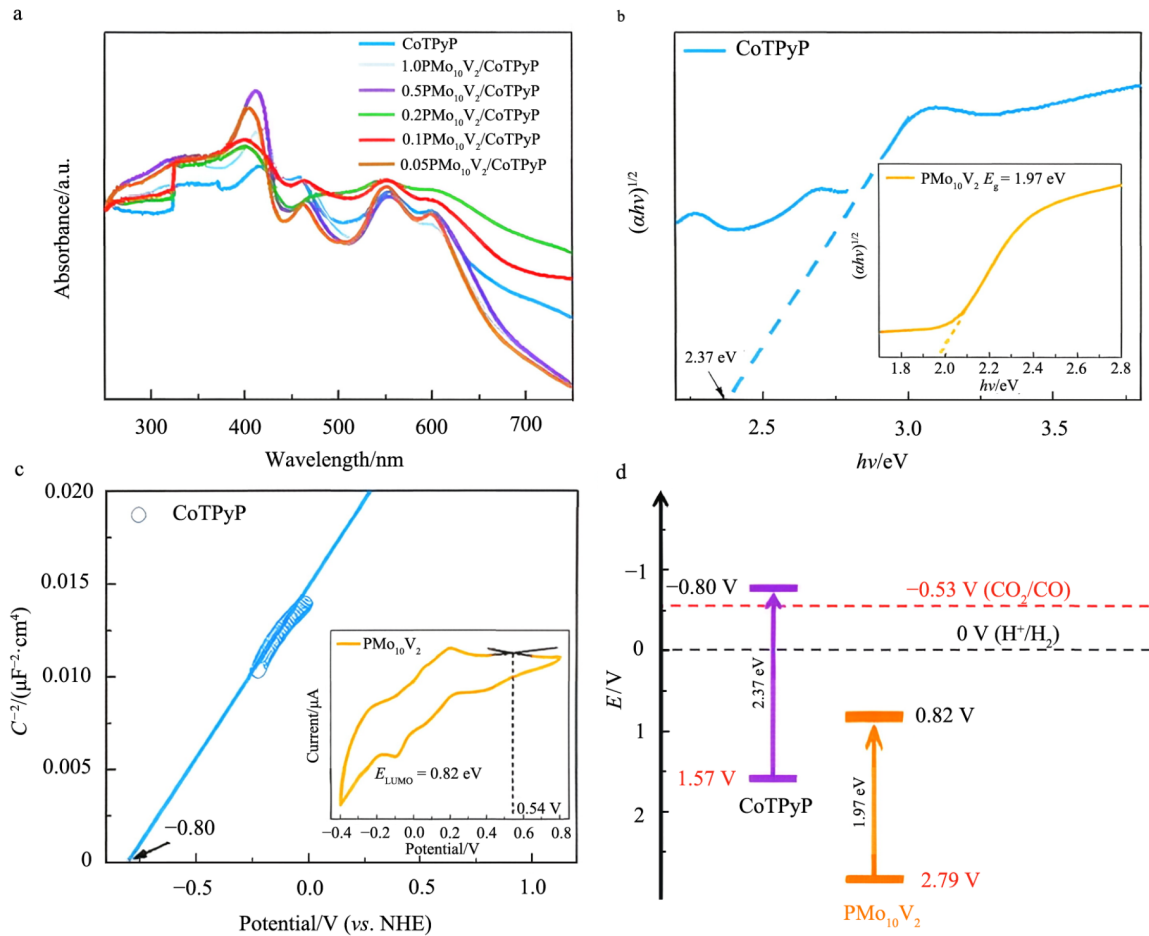


Figure 4 UV-Vis diffuse reflectance spectra of CoTPyP and γ -PMo₁₀V₂/CoTPyP (a), Kubelka-Munk transformed reflectance spectra of CoTPyP and PMo₁₀V₂ (b), Mott-Schottky plot of CoTPyP and cyclic voltammetry (CV) curve of PMo₁₀V₂ (c), and proposed energy band alignment diagram for CoTPyP and PMo₁₀V₂ (d)

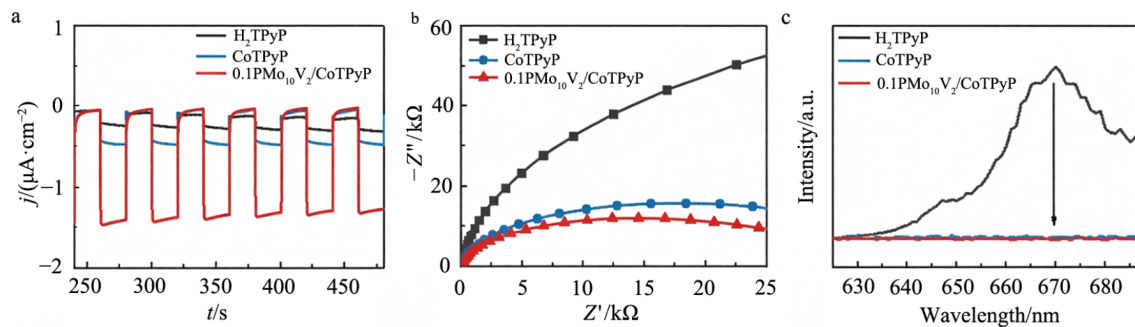


Figure 5 Photocurrent response spectra (a), electrochemical impedance spectra (b), and steady-state photoluminescence (PL) spectra (c) of H₂TPyP, CoTPyP, and 0.1PMo₁₀V₂/CoTPyP

samples under visible light irradiation ($\lambda \geq 420 \text{ nm}$). The 0.1PMo₁₀V₂/CoTPyP heterojunction exhibited a photocurrent density of approximately $1.47 \mu\text{A}\cdot\text{cm}^{-2}$, which is about 3.1 and 6.7 times higher than that of CoTPyP ($0.48 \mu\text{A}\cdot\text{cm}^{-2}$) and H₂TPyP ($0.21 \mu\text{A}\cdot\text{cm}^{-2}$), respectively. This result further confirms that the formation of the heterojunction effectively promotes the separation of photo-generated charge carriers. As shown in the electrochemical impedance spectra (EIS) in Figure 5b, the 0.1PMo₁₀V₂/CoTPyP heterojunction displays a smaller arc radius in the

Nyquist plot, indicating a higher charge transfer efficiency compared to the other samples. The steady-state photoluminescence (PL) spectra (See Figure 5c) reveal a strong and broad emission peak at around 670 nm for H₂TPyP. In contrast, both CoTPyP and 0.1PMo₁₀V₂/CoTPyP show significantly quenched PL intensity at the same wavelength, suggesting suppressed radiative recombination of photo-generated electron-hole pairs. This PL quenching can be attributed to the efficient interfacial charge transfer within the heterojunction, which greatly enhances the separation

efficiency of photogenerated carriers.

2.4 Photocatalytic CO₂ reduction performance

The photocatalytic CO₂ reduction performance of the synthesized heterojunction catalysts was evaluated in an aqueous system under ambient temperature and pressure. The reaction utilized CO₂ generated *in-situ* from the reaction between Na₂CO₃ and HCl as the carbon source, with triethanolamine (TEOA) employed as a sacrificial agent. Under simulated solar irradiation ($\lambda \geq 420$ nm), chromatographic analysis confirmed that the selectivity for CO as the reduction product exceeded 99%. To elucidate the essential

roles of various components in the photocatalytic CO₂ reduction process, the performance of 0.1PMo₁₀V₂/CoTPyP was evaluated under different reaction conditions. As shown in Figure 6a, no CO was detected in the absence of the photocatalyst, light irradiation, sacrificial agent, or carbon source, demonstrating that all these components are essential for the CO₂ reduction reaction. Furthermore, to confirm the origin of the exclusive reduction product CO, a ¹³C isotopic labeling experiment was conducted in a ¹³CO₂ atmosphere using 0.1PMo₁₀V₂/CoTPyP. The appearance of a distinct signal at $m/z = 29$ in the GC-MS spectrum (See Figure 6b) provides clear evidence that the produced CO originates from CO₂ in the system, rather than from the

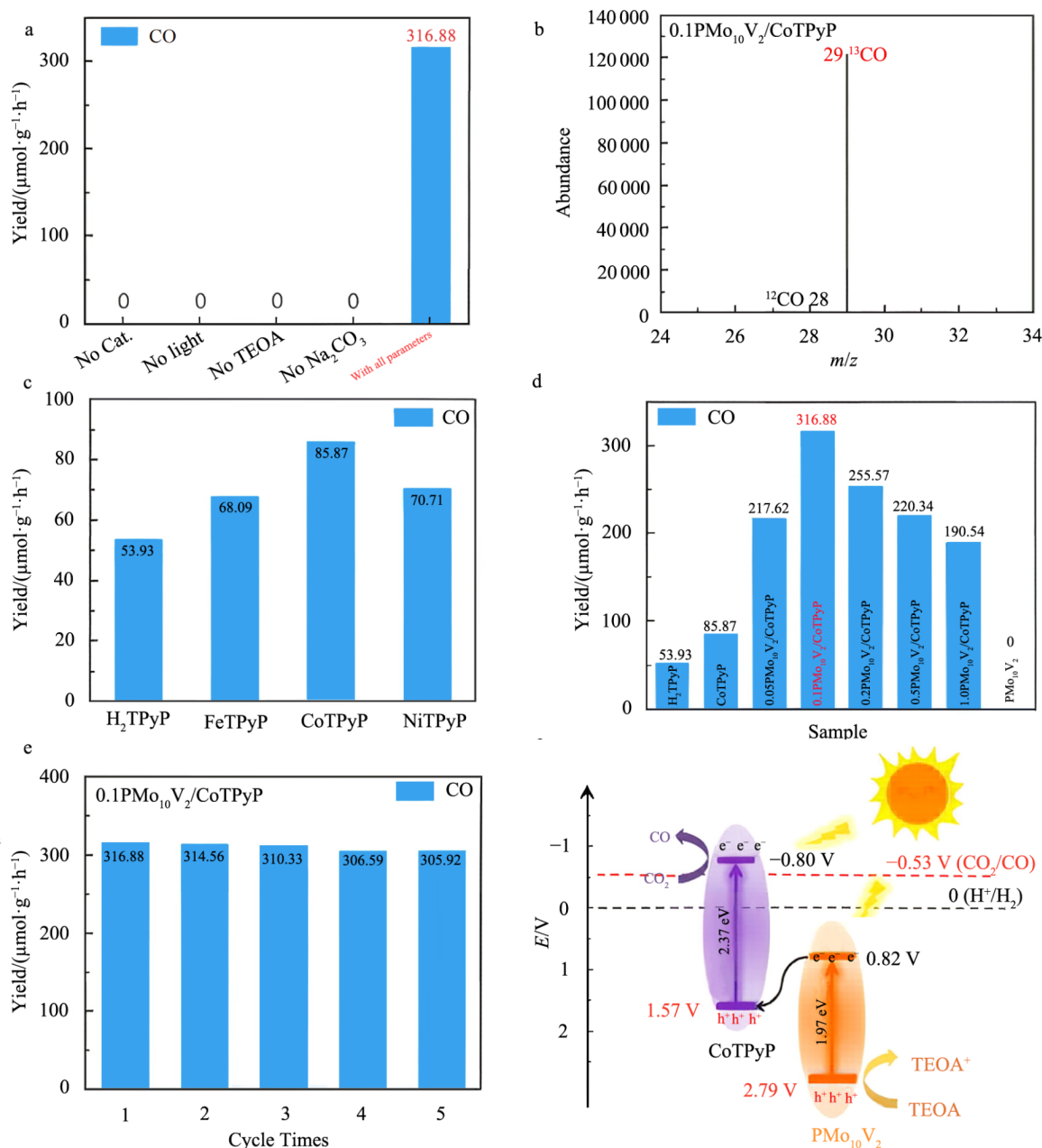


Figure 6 Photocatalytic performance under different conditions (a), GC-MS results of the ¹³C isotope labeling experiment of 0.1PMo₁₀V₂/CoTPyP (b), photocatalytic activities of H₂TPyP and TMTPyP (c), comparison of photocatalytic performance among H₂TPyP, CoTPyP, yPMo₁₀V₂/CoTPyP, and PMo₁₀V₂ (d), stability test (e), and proposed electron transfer pathway of 0.1PMo₁₀V₂/CoTPyP for photocatalytic CO₂ reduction (f)

decomposition of TEOA or the heterojunction photocatalyst itself.

The influence of different transition metals on the photocatalytic CO₂ reduction performance was investigated. The photocatalytic performance of H₂TPyP and TMTPyP (TM = Fe, Co, Ni) was evaluated, and the results are shown in Figure 6c. Compared with the pristine H₂TPyP, the transition metal-incorporated metalloporphyrins TMTPyP exhibited varying degrees of enhanced reactivity. Among them, CoTPyP demonstrated the best performance, with a CO production rate of 85.87 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is 1.6 times higher than that of the pristine H₂TPyP (53.93 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), while maintaining a selectivity of >99%. Subsequently, the photocatalytic CO₂ reduction performance of the PMo₁₀V₂ composites was evaluated. No CO generation was detected. This is attributed to the fact that the conduction band energy of PMo₁₀V₂ is more positive than the redox potential required for reducing CO₂ to CO. As shown in Figure 6d, the photocatalytic CO₂ reduction activity of the yPMo₁₀V₂/CoTPyP heterojunctions exhibits an initial increase followed by a decrease as the PMo₁₀V₂ loading is progressively increased. The optimal activity was observed for the 0.1PMo₁₀V₂/CoTPyP heterojunction, which exhibited a CO production rate of 316.88 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. This rate is 3.7 times and 5.9 times higher than those of CoTPyP and pristine H₂TPyP. Furthermore, the 0.1PMo₁₀V₂/CoTPyP heterojunction showed outstanding stability, maintaining a CO production rate of 305.92 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with a selectivity exceeding 99% over five recycling tests (See Figure 6e).

Based on the band positions of CoTPyP and PMo₁₀V₂, the electron transfer pathway in the 0.1PMo₁₀V₂/CoTPyP heterojunction during photocatalytic CO₂ reduction was proposed^[24-26], as illustrated in Figure 6f. The CB potential of CoTPyP is higher than the redox potential for CO₂ reduction to CO, while that of PMo₁₀V₂ is significantly lower. As a result, PMo₁₀V₂ alone cannot drive the photocatalytic CO₂ reduction, indicating that the active sites in the 0.1PMo₁₀V₂/CoTPyP heterojunction are located on CoTPyP. The remarkable enhancement in photocatalytic activity after forming the heterojunction with PMo₁₀V₂ suggests that the electron transfer follows a Z-scheme mechanism, rather than a conventional type-II heterojunction that typically compromises reduction capability. Under light irradiation, both CoTPyP and PMo₁₀V₂ are excited to generate electron-hole pairs. Owing to the highly oxidative HOMO of PMo₁₀V₂, the photogenerated holes on its HOMO rapidly react with the hole scavenger TEOA in the system and get consumed. This process greatly suppresses the recombination of electron-hole pairs in PMo₁₀V₂. Meanwhile, the photogenerated electrons on the LUMO of PMo₁₀V₂ quickly migrate to the VB of CoTPyP due to their close band alignment, thereby quenching the photogenerated holes in the VB of CoTPyP. This further inhibits the radiative recombination of photogenerated charges in CoTPyP, leaving highly reductive electrons in the CB of CoTPyP to drive the CO₂ reduction

reaction. This electron transfer pathway is analogous to the Z-scheme mechanism in the light reaction phase of plant photosynthesis, which accounts for the excellent photocatalytic CO₂ reduction activity observed.

3. Conclusion

In summary, a series of bio-inspired Z-scheme heterojunction photocatalysts yPMo₁₀V₂/CoTPyP were successfully constructed by integrating metalloporphyrin CoTPyP with polyoxometalate PMo₁₀V₂ through supramolecular self-assembly. The optimized 0.1PMo₁₀V₂/CoTPyP heterojunction exhibited significantly enhanced photocatalytic CO₂ reduction activity, achieving a CO production rate of 316.88 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ with over 99% selectivity, which was 3.7 times and 5.9 times higher than those of pristine CoTPyP and H₂TPyP, respectively. Systematic characterization revealed that the enhanced performance originates from the Z-scheme electron transfer mechanism, which effectively promotes charge separation while preserving the strong reduction ability of CoTPyP. This work provides a feasible strategy for mimicking natural photosynthesis at the molecular level and offers valuable insights for the rational design of efficient artificial photosynthetic systems. The supporting information, including detailed synthetic procedures for H₂TPyP, TMTPyP, and yPMo₁₀V₂/CoTPyP, as well as descriptions of photocatalytic CO₂ reduction tests, electrochemical measurements, SEM images of H₂TPyP and TMTPyP, nitrogen adsorption-desorption isotherms of H₂TPyP, and TEM elemental mapping of 0.1PMo₁₀V₂/CoTPyP, is available free of charge at <https://doi.org/10.3724/jmolsci.2025110007>.

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金属卟啉与 $\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 34.5\text{H}_2\text{O}$ 复合催化剂的合成及光催化 CO_2 还原

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摘要 受叶绿素结构启发, 以金属卟啉CoTPyP和磷钼钒酸($\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]\cdot 34.5\text{H}_2\text{O}$)为构筑单元, 成功构建了一系列仿生Z型异质结光催化剂 $\text{yPMo}_{10}\text{V}_2/\text{CoTPyP}$ 。其中性能最优的0.1 $\text{PMo}_{10}\text{V}_2/\text{CoTPyP}$ 复合材料在光催化 CO_2 还原中表现出显著增强的活性, 其 CO 生成速率达到 $316.88\ \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, 分别为单一CoTPyP和 H_2TPyP 的3.7倍和5.9倍。系统表征结果表明, 该体系遵循Z型电子转移路径, 不仅大幅提升了电荷分离效率, 同时有效保留了材料的高氧化还原能力。本研究从分子层面验证了模拟自然光合作用的可行策略, 为设计高效人工光合系统提供了新思路与实验依据。

关键词 金属卟啉; 多金属氧酸盐; 光催化 CO_2 还原; Z型异质结