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Photocatalytic CO₂ Reduction Enabled by Interfacial S-scheme

Heterojunction between Ultra-Small Copper Phosphosulfide and g-C₃N₄

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Abstract

Transition metal phosphosulfides (TMPSs) have gained much interest due to their highly enhanced photocatalytic activities compared with their corresponding phosphides and sulfides. However, the application of TMPSs on photocatalytic CO₂ reduction remains a challenge due to their inappropriate band positions and rapid recombination of photogenerated electron–hole pairs. Herein, we report ultra-small copper phosphosulfide (us-Cu₃P|S) nanocrystals anchored on 2D g-C₃N₄ nanosheets. Systematic studies on the interaction between us-Cu₃P|S and g-C₃N₄ indicate the formation of an S-scheme heterojunction *via* interfacial P–N chemical bonds, which acts as an electron transfer channel and facilitates the separation and migration of photogenerated charge carriers. Upon the composite formation, the band structures of us-Cu₃P|S and g-C₃N₄ are altered to enable the enhanced photocatalytic CO generation rate of 137 µmol g⁻¹ h⁻¹, which is eight times higher than that of the pristine g-C₃N₄. The unique phosphosulfide structure is also beneficial for the enhanced electron transfer rate and provides abundant active sites. This first application of Cu₃P|S to photocatalytic CO₂ reduction marks an important step toward the development of TMPSs for photocatalytic applications.

1. Introduction

With high gravimetric energy densities, fossil fuels have been the major energy source for modern society.¹⁻² However, the soaring global energy demands have driven the excessive use of fossil fuels, which inevitably led to severe climate changes due to the unwanted side-production of greenhouse gases such as carbon dioxide (CO₂). Conversion of CO₂ to high-energy compounds or value-added chemicals by solar light has aroused much interest as a renewable and sustainable way to abate pollution problems as well as to relieve concerns on the depletion of fossil fuels.³⁻⁴

To date, intensive effort has been devoted to developing efficient photocatalysts that can effectively catalyze the energetically uphill CO₂ reduction reaction.⁵⁻⁸ Recently, transitionmetal phosphosulfides (TMPSs) have received much attention owing to their outstanding performances towards various catalytic reduction reactions.⁹⁻¹¹ It was reported that the unique phosphosulfide (PS) structure could offer more active sites for catalytic reaction with better stability than their corresponding phosphide or sulfide forms.⁹ Molybdenum phosphosulfide (MoP|S), the first reported TMPS, was prepared *via* a two-step route where the Mo salt was annealed with P and S precursors under a high temperature of 650 °C. The MoP|S that pertained MoP crystal structure exhibited a much higher catalytic performance towards hydrogen evolution reaction (HER). Later, cobalt phosphosulfide^{10, 12} and iron phosphosulfide¹¹ grown on substrates were studied as electrocatalysts. The PS structure in TMPSs, regardless initial base crystal structure, were shown to be responsible for good catalytic HER activities. So far, the development of these novel PS structures is limited to a few transition metals, mainly due to harsh synthetic conditions. Among this relatively new class of phosphosulfides, none of them has been applied toward photocatalytic CO₂ reduction yet. Recently, we prepared a freestanding copper phosphosulfide (Cu₃P|S) nanoplates under relatively mild synthetic conditions and engaged them as an HER photocatalyst. The PS structure in Cu₃P|S drives the Gibbs free energy (ΔG_{H^*}) of atomic hydrogen adsorption close to 0 eV and provides more active sites than the original Cu₃P, which leads to much enhanced photocatalytic HER performance. These Cu₃P|S nanoplates, however, easily aggregate in the reaction reagent, resulting in a declined photocatalytic performance in long-term reactions. More importantly, the fast recombination of charge carriers and inappropriate band position of Cu₃P|S nanoplates prevent their application toward photocatalytic CO₂ reduction.

Herein, ultra-small copper phosphosulfide (us-Cu₃P|S) nanocrystals were designed and coupled with 2D g-C₃N₄ to form an S-scheme composite. By controlling the amount of trioctylphosphine, which is used as a capping ligand, the dimension of us-Cu₃P|S is effectively constrained and the aggregation of nanocrystals is prevented. 2D g-C₃N₄ nanosheet provides a large surface area with abundant function groups to allow the intimate interaction with us-Cu₃P|S to form us-Cu₃P|S/2D g-C₃N₄ composite (us-Cu₃P|S/CN). Upon the formation of the composite, electron transfer route is rearranged at the heterojunction, suppressing the charge recombination, and thereby enabling photocatalytic CO₂ reduction on us-Cu₃P|S. The nature and role of the heterojunction between us-Cu₃P|S and g-C₃N₄ are systematically investigated to reveal the photocatalytic CO₂ reduction mechanism of us-Cu₃P|S/CN. The factors contributing to the enhanced catalytic activity are also discussed in detail.

2. Experimental section

2.1. Materials and chemicals

Sodium hypophosphite monohydrate (NaH₂PO₂·H₂O, 99 %) and elemental sulfur (S, 99.98 %) were purchased from Uni-Chem. Cuprous chloride (CuCl, 99.99 %), trioctylphosphine oxide (TOPO, 90 %), oleylamine (OLA, 70 %), trioctylphosphine (TOP, 97 %), Nafion[®] 117 solution (5 wt.%), acetonitrile (99 %), and ethyl acetate (99 %) were purchased from Sigma Aldrich. All chemicals and solvents were used as received unless stated otherwise.

2.2. Synthesis of ultra-small Cu₃P and Cu₃P|S nanocrystals

Ultra-small Cu₃P (us-Cu₃P) nanocrystals were synthesized based on the previous report with slight modifications.¹⁴ Briefly, CuCl (0.15 g) and TOPO (1 g) were dissolved in OLA (10 mL) and heated to 110 °C under N₂ gas for 15 min. To the reaction mixture, TOP (5 mL) was injected and temperature was raised to 150 °C. Then, PH₃ gas that was separately generated by heating NaH₂PO₂ (0.8 g) at 250 °C was purged into the reaction mixture at 230 °C under N₂ flow for 1 h. After cooling down to room temperature, the reaction mixture was centrifuged and washed with hexane and acetone repeatedly to yield a solid product. Ultra-small Cu₃P|S (us-Cu₃P|S) nanocrystals were prepared in a similar method. After the reaction with PH₃, a sulfur solution containing of 0.3 g of elemental S in 3 mL OLA was added to the reaction mixture.

2.3. Synthesis of us-Cu₃P/CN and us-Cu₃P|S/CN composites

2D g-C₃N₄ (g-C₃N₄) was first synthesized by a solid-state method following the literature procedure.¹³ Then, the g-C₃N₄ (40 mg) was dispersed in hexane (20 mL) and sonicated for 30 min. In a separate round-bottomed flask, the as-synthesized us-Cu₃P or us-Cu₃P|S (12 mg, 30 wt.%) was added to hexane (10 mL) and sonicated for 30 min. To this us-Cu₃P or us-Cu₃P|S dispersion, the g-C₃N₄ suspension was added and sonicated for another hour. The products

were collected after completely drying (denoted as us-Cu₃P/CN or us-Cu₃P|S/CN, respectively). A physical mixture of us-Cu₃P|S and g-C₃N₄ was prepared for comparison. In a typical procedure, us-Cu₃P|S (12 mg) and g-C₃N₄ (40 mg) were dispersed in hexane (20 mL), respectively, and sonicated for 1.5 h in separate tubes. Then, us-Cu₃P|S and g-C₃N₄ powders were mixed together after drying and denoted as p-Cu₃P|S/CN.

2.4. Characterization of Materials

Transmission electron microscopy (TEM) was conducted on a JEOL system (JEM-2100 F STEM, 200 eV). For TEM analysis, the catalyst ink was prepared by dissolving the as-prepared samples in hexane. The elemental mappings of samples were collected under STEM mode. Powder X-ray diffraction (PXRD) patterns were obtained on an X-ray diffractometer (Rigaku SmartLab) with Cu K α radiation. The specific surface area and carbon dioxide (CO₂) adsorption measurement were conducted by an automatic micropore and chemisorption physisorption analyzer (ASAP 2020, Micromeritics). Raman spectra were collected on a confocal micro-Raman spectroscopy system (Renishaw, inVia) with a 785nm stream-line laser excitation. Fourier-transform infrared spectra (FTIR) were acquired using a Thermo Electron Corporation Fourier-transform spectrophotometer (Nexus 470). X-ray photoelectron spectroscopy (XPS) was conducted on an X-ray photoelectron spectrometer (Thermo Fisher, Nexsa) with a monochromic Al Ka X-ray source. The obtained XPS data were treated with the CasaXPS software with a Spline Shirley type of background and peak profile of Gaussian-Lorentzian GL(30). Ultraviolet photoelectron spectroscopy (UPS) was carried out on the same spectrometer (He I, 21.2 eV). UV-vis diffuse reflectance spectra (UV-vis DRS) were measured on a Cary 4000 UV-vis spectrophotometer. Photoluminescence spectra were collected on an

Edinburgh fluorescence spectrophotometer (FLS1000) using a Xenon lamp as a light source with an excitation at 325 nm. Time-resolved photoluminescence spectra were obtained on the same fluorescence spectrophotometer with a 375 nm-laser as the excitation light source. A biexponential kinetic function was used to fit the curve after obtaining the response function (IRF) of instrument, using the equation, $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 is the short lifetime, τ_2 is the long lifetime, and A_1 and A_2 are the corresponding amplitudes. To assure the fitting level, the Chi-square, χ^2 , was kept between 1 and 1.3.

2.5. Photocatalytic CO₂ reduction reaction

All the photocatalytic reactions were carried out in a closed system using a 50 mL Pyrex reaction cell. First, the catalyst (5 mg) was dispersed in a solution containing 20 mL acetonitrile or ethyl acetate and 500 µL DI water. The catalyst suspension was sonicated for 5 min and degassed with high purity CO₂ for 30 min. A 300 W xenon lamp (Ceaulight, 1 sun) was used as the light source. An Agilent 7890 B gas chromatograph system equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used to detect gaseous products. For the analysis of liquid products, ¹H nuclear magnetic resonance spectroscopy (NMR, Bruker Advance-III). The stability of catalysts was tested by conducting five consecutive 2-hour reactions in both acetonitrile/H₂O and ethyl acetate/H₂O solvent systems. Before each run, the reactor was refilled with CO₂ for 30 min without adding additional catalysts.

2.6. Electrochemical measurements

The catalyst ink was prepared by completely dispersing the as-prepared catalyst (5 mg) in a mixture of 300 μ L ethanol, 200 μ L DI water, and 40 μ L Nafion solution (0.5 wt.%) by

sonication. Then, 100 μ L of as-prepared ink was drop-cast onto a square Ni foam (1 × 1 cm²) and air-dried overnight, and used as a working electrode. Linear sweep voltammograms (LSV) and electrochemical impedance spectra (EIS) were collected on a CHI 700E electrochemical station (Chenhua Instrument) in a three-electrode configuration using Pt foil and saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. The electrochemical measurements were conducted in a phosphate buffer (pH = 7.4).

3. Results and discussion





Figure 1. TEM images of (a) us-Cu₃P, (b) us-Cu₃P|S, (c) us-Cu₃P/CN, and (d) us-Cu₃P|S/CN. Insets in (a-d) are the corresponding HRTEM images. (e) XRD patterns of us-Cu₃P, us-Cu₃P|S, g-C₃N₄, us-Cu₃P/CN, and us-Cu₃P|S/CN.

Ultra-small copper phosphosulfide (us-Cu₃P|S) nanocrystals were prepared by a wet-chemical method. During the synthesis of ultra-small copper phosphide (us-Cu₃P), elemental S was introduced to create homogeneous phosphosulfide (PS) structures (**Scheme S1**).¹⁴ It is essential to precisely control the ratio of Cu precursor (CuCl) and capping ligand (trioctylphosphine, TOP) for tuning the product size. The excess addition of TOP increases the amount of Cu-

oleylamine complex, which in turn creates more nucleation sites,¹⁵ leading to the production of ultra-small Cu₃P and Cu₃P|S crystals (see details in the Experimental section). The amount of S incorporated into the us-Cu₃P|S is 21.6 % as suggested by the energy dispersive spectra (EDS, **Figure S1**). This doping level was chosen for the optimal photocatalytic activity based on our previous investigation.¹⁴ The as-prepared us-Cu₃P|S nanocrystals (30 wt.%) were sonicated together with 2D g-C₃N₄ in hexane to form a composite of us-Cu₃P|S embedded on g-C₃N₄ (us-Cu₃P|S/CN). Two control samples, us-Cu₃P coupled with g-C₃N₄ (us-Cu₃P/CN) and a physical mixture of g-C₃N₄ and us-Cu₃P|S (p-Cu₃P|S/CN), were also prepared for comparison.

Transmission electron microscopy (TEM) was employed to analyze the structure and morphology of the as-prepared samples. Both us-Cu₃P and us-Cu₃P|S show a well-defined morphology of rounded hexagonal nanocrystals with monodispersed size distributions (**Figure 1a** and **1b**). The average diameter of us-Cu₃P|S (9.8 \pm 3.2 nm) is similar to that of us-Cu₃P (10.6 \pm 3.5 nm), suggesting that the particle size is unaltered by PS structure formation. The TEM image of g-C₃N₄ displays several thin layers of nanosheet morphology (**Figure S2a**). **Figure 1c** and **1d** confirm that us-Cu₃P and us-Cu₃P|S nanocrystals are embedded on the g-C₃N₄ nanosheet without any aggregation. The lattice *d*-spacing of 2.02 Å for (300) plane are clearly observable in the high-resolution (HR-TEM) images of all samples (insets in **Figure 1a-d**), suggesting that the Cu₃P crystal structure is retained during the formation of PS structure, as well as the hybridization with g-C₃N₄. This is also supported by their X-ray diffraction (XRD) patterns (**Figure 1e**) that exhibit its characteristic peaks at 36.1°, 39.2°, 41.8°, 45.1°, and 46.5°, which match the (112), (202), (211), (300), and (113) planes of Cu₃P (PDF# 02-1263), respectively.¹⁵ An additional peak at 27.8°, which corresponds to the (002) lattice planes of g C_3N_4 , is identified from us-Cu₃P/CN and us-Cu₃P|S/CN,¹⁶ confirming the formation of highly crystalline composites. The 2D structure of g-C₃N₄ and small particle size of us-Cu₃P|S are advantageous for achieving a large surface area. The surface area analysis by Brunauer–Emmett–Teller (BET) method indicates a slightly increased surface area of us-Cu₃P|S/CN (149.37 m² g⁻¹) compared with that of us-Cu₃P|S (139.21 m² g⁻¹). Both g-C₃N₄ and us-Cu₃P|S/CN exhibit a good CO₂ adsorption ability with a fast increase of CO₂ adsorption in the low-pressure region (0 < P/P₀ < 1), suggesting a chemisorption of CO₂ from the surface functional groups¹⁷ (**Figure S2b**). The overall CO₂ adsorption capacity of g-C₃N₄ is higher than that of us-Cu₃P|S/CN, implying a possible interaction between us-Cu₃P|S/CN and the functional groups on g-C₃N₄.

3.2. Interface structure of us-Cu₃P/S/C₃N₄ and us-Cu₃P/CN composites

Raman and Fourier-transform infrared (FTIR) spectroscopy were engaged to investigate the interfacial interactions in us-Cu₃P/CN and us-Cu₃P|S/CN composites. The us-Cu₃P|S/CN exhibits Raman peaks at 470, 707, 978, 1230, and 1310 cm⁻¹, which are attributed to the inplane twisting vibration of heptazine heterocycle, breathing mode of *s*-triazine ring, bending vibration of =C (sp²), and C–N stretching vibration of terminal amide groups, respectively (**Figure 2a**). Similar peaks are observed from us-Cu₃P/CN, p-Cu₃P|S/CN, and g-C₃N₄. However, the peaks at 1230 and 1310 cm⁻¹ show an obvious negative shift of 0.3° in the us-Cu₃P/CN and us-Cu₃P|S/CN composites compared with the pristine g-C₃N₄ and p-Cu₃P|S/CN, suggesting possible chemical interactions of g-C₃N₄ with us-Cu₃P and us-Cu₃P|S/CN are also observed from the FTIR spectra presented in **Figure 2b**. All four samples display the characteristic peaks of

g-C₃N₄, including the triazine ring at 807 cm⁻¹, stretching modes of aromatic C–N and C=N bonds at $1200 - 1650 \text{ cm}^{-1}$,¹⁹ and surface –NH_x amino groups attached on the g-C₃N₄ at 3000 – 3500 cm⁻¹.²⁰ Notably, a weak peak at 950 cm⁻¹ assigned as P–N bond¹⁹ is identified only from us-Cu₃P/CN and us-Cu₃P|S/CN, which echoes the observations in Raman spectra.



Figure 2. (a) Raman and (b) FTIR spectra of us-Cu₃P/S/CN, us-Cu₃P/CN, p-Cu₃P/S/CN, and g-C₃N₄.



Figure 3. XPS spectra in (a) C 1s and (b) N 1s regions of us-Cu₃P|S/CN, us-Cu₃P/CN, p-Cu₃P|S/CN, and g-C₃N₄. XPS spectra in (c) P 2p, (d) Cu 2p, and (e) S 2p regions of us-Cu₃P|S/CN, us-Cu₃P/CN, us-Cu₃P|S, and us-Cu₃P.

X-ray photoelectron spectroscopy (XPS) was used to probe the surface composition and electronic configuration. The survey XPS spectra shown in **Figure S3** confirm the existence of C, N, Cu, P, and S elements in us-Cu₃P|S/CN. The C 1s XPS spectra of g-C₃N₄ and its composites (us-Cu₃P/CN and us-Cu₃P|S/CN) as well as the physical mixture (p-Cu₃P|S/CN) exhibit three main peaks at 284.6, 286.2, and 288.0 eV, which arise from the C–C species in impurities, C–NH_x, and N–C=N species of g-C₃N₄, respectively (**Figure 3a**).²¹ In N 1s region (**Figure 3b**), four typical peaks of g-C₃N₄ are observed at 398.4, 399.7, 400.1, and 404.2 eV, which correspond to the C–N=C species, N–(C)₃ species, –NH_x from functional amino-group, and π -excitation in heterocycles, respectively.²⁰ It is worth noting that the –NH_x peaks in both us-Cu₃P/CN and us-Cu₃P|S/CN composites are negatively shifted by 0.3 eV, which strongly suggests the electron redistribution on the N atoms of amino group. In contrast, such shift is not observed from the physical mixture of g-C₃N₄ and Cu₃P|S. An opposite peak shift is noted

in the P 2p region XPS spectra of us-Cu₃P/CN and us-Cu₃P|S/CN. Both us-Cu₃P and us-Cu₃P|S nanocrystals exhibit two characteristic peaks at 129.4 and 133.5 eV, which arise from the P³⁻ species (Cu–P) and surface oxygen species (P–O), respectively (**Figure 3c**, purple lines).²² Upon the composite formation with g-C₃N₄, the P³⁻ peaks are positively shifted by 0.2 eV (**Figure 3c**, green lines). The position of surface oxygen peaks, however, remain unchanged. This implies that an electron-deficient environment is built on the P atoms in Cu–P, which can be compensated with the electron-rich N atoms in $-NH_x$ by forming a covalent P(δ^+)–N(δ^-) bonding state,²³ as also suggested by the FTIR analyses.

The XPS spectra in Cu 2p and S 1s regions confirm the PS structure in us-Cu₃P|S/CN (**Figure 3d** and **e**). The Cu 2p spectra of us-Cu₃P, us-Cu₃P|S, and their composites with g-C₃N₄ display a pair of Cu $2p_{3/2}$ and $2p_{1/2}$ peaks at 932.5 and 952.2 eV, respectively, which can be assigned to the Cu⁺ species of Cu–P bonds.²⁴ Another two peaks at 934.7 and 954.2 eV are only observed from us-Cu₃P|S and us-Cu₃P|S/CN, which are attributed to the Cu²⁺ species in Cu–S bonds in the PS structure.¹⁴ Meanwhile, the S 2p spectra of us-Cu₃P|S and us-Cu₃P|S/CN are similar. The two peaks at 161.8 and 163.1 eV in the S $2p_{3/2}$ and S $2p_{1/2}$ regions, respectively, are assigned to the S²⁻ species in Cu–S bonds, confirming the PS structure.^{9, 14}



Figure 4. Photocatalytic CO production rates of us-Cu₃P, us-Cu₃P|S, g-C₃N₄, us-Cu₃P/CN, and us-Cu₃P|S/CN in (a) acetonitrile/H₂O and (b) ethyl acetate/H₂O solvent systems. Error bars were calculated based on multiple measurements using the same samples from different synthetic batches. (c) Stability test of us-Cu₃P|S/CN in a five consecutive 2-hour photocatalytic reactions. (d) Photocatalytic CO production rates under various conditions.

3.3 Photocatalytic performance on CO₂ reduction

Photocatalytic CO₂ reduction reaction (CRR) was carried out to investigate the impact of us-Cu₃P|S/CN formation. Two mixed solvents, acetonitrile/H₂O and ethyl acetate/H₂O (20 mL/500 μ L), which have better CO₂ solubility than pure water and are known to suppress the competing hydrogen evolution reaction, were chosen as the reaction medium.²⁰ In both reaction media, CO was the main reduction product with no H₂ or other CRR products detected. In the acetonitrile/H₂O mixture, the recorded CO production rate of g-C₃N₄ is low (17 μ mol g⁻¹ h⁻¹, **Figure 4a**), which is in agreement with previous reports.²⁵ No products were detected when us-Cu₃P or us-Cu₃P|S was used alone, suggesting their restricted catalytic activity toward CRR. However, both us-Cu₃P/CN and us-Cu₃P|S/CN composites show impressive promotional effects on the CO generation rate. Particularly, the CO generation rate of us-Cu₃P|S/CN reaches 137 μ mol g⁻¹ h⁻¹, which exceeds an eight-fold increase compared with that of the pristine g-C₃N₄. The same trend of CO production rate is observed when the catalytic reactions were conducted in the ethyl acetate/H₂O mixture (**Figure 4b**). Although the CO production rates for all the evaluated catalysts are lower than those in acetonitrile/H₂O solution, the photocatalytic activities of us-Cu₃P/CN and us-Cu₃P|S/CN composites are still remarkably improved. The us-Cu₃P|S/CN achieves the CO generation rate of 96 μ mol g⁻¹ h⁻¹, which is also eight times higher than that of the pristine g-C₃N₄ (12 μ mol g⁻¹ h⁻¹). In the five consecutive 2-hour runs, the us-Cu₃P|S/CN composite also delivers a steady CO production rate in both solvent systems without any apparent loss of activity (**Figure 4c**).

Several control experiments were performed to ensure the results of photocatalytic CO production of catalysts (**Figure 4d**). A simple physical mixture of $Cu_3P|S$ and g- C_3N_4 , p- $Cu_3P|S/CN$, shows a similar CO production rate as the pristine g- C_3N_4 , suggesting the crucial role of P–N chemical bonding in boosting CRR catalysis. Other control experiments that were conducted without CO₂ (by replacing CO₂ with Ar) or solar irradiation result in no product generation, confirming that CO is generated by photocatalytic CO₂ reduction reaction. The TEM image and XRD pattern of us-Cu₃P|S/CN obtained after photocatalytic reaction show unaltered morphology and crystallinity, demonstrating its good stability. (**Figure S4**).

3.4. Mechanism of photocatlytic CO₂ reduciton

The electronic structure of composites were investigated to unveil the mechanism of

photocatalytic CO₂ reduction. The UV-vis diffuse reflectance spectrum (UV-vis DRS) of the pristine g-C₃N₄ (Figure 5a) exhibits a typical adsorption edge at *ca*.430 nm, which reflects its band gap (E_g) of 2.85 eV (Figure 5b, top).¹⁶ Similar spectra showing a broad absorption between 400 and 780 nm were observed from us-Cu₃P and us-Cu₃P|S. Their Tauc plots yield 1.52 eV as the estimated band gap (Figure 5b, bottom).²⁶ The features of both components are evident in the composites. Both us-Cu₃P/CN and us-Cu₃P/S/CN display an obvious absorption tail in visible light region with the absorption edges similar to that of g-C₃N₄. The band positions of g-C₃N₄ and us-Cu₃P|S are further analyzed by ultraviolet photoelectron spectroscoty (UPS) and presented in Figure 5c. The work functions (Φ) of g-C₃N₄ and us-Cu₃P|S were estimated as 3.93 and 5.16 eV (vs. vacuum), respectively, which were obtained from the beginning of the secondary photoemission (E_{cutoff}) using Equation (1).²⁷ Thus, the Fermi levels (E_F) of g-C₃N₄ and us-Cu₃P|S were calculated to be -0.92 and 0.31 V, respectively, against the normal hydrogen electrode (NHE) at pH = 7 using Equtation (2). In addition, using VB-XPS, their corresponding valence band positions (E_{VB}) were estimated as 1.73 and 0.81 V (Figure S5a) based on $E_{\text{NHE}} = \Phi + 1.82$ (or 0.90) – 4.44 (Φ , the electron work function of the analyzer, is 4.35 eV).²⁵ Combining the band gap obtained from UV-vis DRS, the conduction bands (E_{CB}) of g-C₃N₄ and us-Cu₃P|S were calculated as -1.12 and -0.71 V using Equation (4).

$$hv (\text{He}, 21.22 \text{ eV}) = E_{\text{cutoff}} + \Phi$$
(1)

$$E (vs. \text{ NHE, pH} = 7) = -4.44 - E (vs. \text{ vacuum level}) - 0.059 \text{ pH}$$
 (2)

$$E_{\rm VB} = E_{\rm edge} + \Phi \tag{3}$$

$$E_{\rm CB} = E_{\rm VB} - E_{\rm g} \tag{4}$$



Figure 5. (a) UV–vis DRS spectra of us-Cu₃P, us-Cu₃P|S, g-C₃N₄, us-Cu₃P/CN, and us-Cu₃P|S/CN. (b) The corresponding Tauc plots and (c) UPS spectra of g-C₃N₄ and us-Cu₃P|S. (d) Illustration of band structures of us-Cu₃P|S and g-C₃N₄ before composite formation (left) and charge-transfer pathways in the us-Cu₃P|S/CN S-Scheme composite under irradiation (right). (e) Photo-responded ESR spectra of DMPO–•OH (aquous, top) and DMPO–•O₂⁻ (MeOH, bottom) in the presence of g-C₃N₄, us-Cu₃P|S, and us-Cu₃P|S/CN.

With these results, the electronic structures of g-C₃N₄ and us-Cu₃P|S were constructed and presented in **Figure 5d**. The result of UPS (**Figure S5b**) shows that when g-C₃N₄ and us-Cu₃P|S are coupled, the E_F levels of the two components shift to the same energy level of -0.52 V, thereby adjusting the band positions of the us-Cu₃P|S/CN composite as illustrated in **Figure 5d**. Such band alignment of g-C₃N₄ and us-Cu₃P|S allows two possible interfaces, either Sscheme or type-II heterojunction, that would lead to two different electron transfer pathways.²⁸⁻³¹ Because the VB position of us-Cu₃P|S in the composite is located below the O_2/H_2O standard redox pontential, it is possible that g-C₃N₄ carries out the H₂O oxidation reaction while us-Cu₃P|S conducts CO₂ reduction reaction, following the S-scheme meachnism. To verify this postulate, electron spin resonace (ESR) spectra were collected to track down the electron transfer direction. The spectra of DMPO-•OH (**Figure 5e**, top) display no obvious signals from g-C₃N₄ nor us-Cu₃P|S, whereas strong ESR signal appears from us-Cu₃P|S/CN, suggesting that holes are left in the VB of g-C₃N₄ upon composite formation. On the other hand, all three samples exhibit ESR signal in the DMPO-•O₂⁻ spectra (**Figure 5e**, bottom), but the peak intensity is much higher for the us-Cu₃P|S/CN composite, indicating an enhanced reduction ability. Both hole capture experimets match well with the estimated band position and the proposed S-scheme mechanism. During the photocatalytic reaction of the us-Cu₃P|S/CN S-scheme composite, electrons with better reduction ability are left on the CB of us-Cu₃P|S to catalyze the CO generation from CO₂, while the holes are acuumulated at the VB of g-C₃N₄ to drive oxidation reaction.



Figure 6. (a) PL and (b) TRPL spectra of g-C₃N₄, p-Cu₃P|S/CN, and us-Cu₃P|S/CN. (c) LSVs and (d) EIS spectra of g-C₃N₄, us-Cu₃P|S/CN, and us-Cu₃P|S/CN.

3.5. Eletron transfer behaviour in us-Cu₃P|S/CN

The formation of S-scheme composite can effectively promote the photocatalytic kinetics. Photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra of us- $Cu_3P|S/CN$ and its control samples, g- C_3N_4 and p- $Cu_3P|S/CN$, were collected to gain insights into the charge transfer and separation rates. The g- C_3N_4 and p- $Cu_3P|S/CN$ show the same peak at 460 nm in the PL spectra (**Figure 6a**), which corresponds to the light absorption of g- C_3N_4 . The PL intensity of us- $Cu_3P|S/CN$ is, however, dramatically reduced, which can be attributed to the fast electron transfer from g- C_3N_4 to us- $Cu_3P|S$ *via* P–N bonds, thus leading to the promoted charge separation and transportation.²³ The TRPL spectra of the three samples are given in **Figure 6b**, which are fitted with bi-exponential decay function, and the fitting results are summarized in **Table S1** (for details, see Experimental section). It is clear that the decay kinetics of g-C₃N₄ and p-Cu₃P|S/CN are nearly identical. The short lifetime (τ_1) that is related to direct carrier recombination is much shorter for us-Cu₃P|S/CN (1.31 ns) than g-C₃N₄ (2.77 ns). The corresponding fractional contribution (f_1) in us-Cu₃P|S/CN (24.5 %) is also lower than that in g-C₃N₄ (41.3 %), indicating that the electron–hole recombination is successfully suppressed in us-Cu₃P|S/CN.³²⁻³³ More importantly, the fractional contribution (f_2) of long lifetime (τ_2) shows an increase from 58.7 % in g-C₃N₄ to 65.5 % in us-Cu₃P|S/CN. This implies a higher probability for electrons to be engaged in photocatalytic reactions.³² In addition, the rate of electron transfer ($k_{\rm ET}$) from g-C₃N₄ to us-Cu₃P|S in us-Cu₃P|S/CN is calculated as 12.3 × 10¹¹ s⁻¹ according to the equation, $k_{\rm ET} = 1/\tau_{\rm ave}$ (composite) – $1/\tau_{\rm ave}$ (g-C₃N₄),³⁴⁻³⁵ a result that is a magnitude faster than that in p-Cu₃P|S/CN (0.8 × 10¹¹ s⁻¹), which clearly demonstrates the role of P–N chemical bond as an efficient channel for fast electron transfer at the interface.

3.6. Role of phosphosulfide structure

Although us-Cu₃P/CN and us-Cu₃P|S/CN share similar interfacial structure as well as band positions, the photocataltyic performance of us-Cu₃P|S/CN largely exceeds that of us-Cu₃P/CN. It was previously reported that PS structures could be more catalytically active than the corresponding phophide structure.⁹ Our previous study also demonstrated that the PS structure in Cu₃P|S enhanced the electron transfer rate and provided more active sites than the pristine Cu₃P, contributing to the enhanced photocatalytic activity.¹⁴ The role of PS structure in the us-Cu₃P|S/CN composite was investigated by linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). As presented in **Figure 6c**, us-Cu₃P|S/CN requires a lower overpoential (420 mV) to reach the current density of 3 mA cm⁻² compared

with g-C₃N₄ (582 mV) and us-Cu₃P/CN (450 mV), suggesting the higher catalytic activity on the PS structure.³⁶ The Nyquist plots (**Figure 6d**) also indicate the enhanced conductivity and electron transfer rate of us-Cu₃P|S/CN, both of which suggest the contribution of PS structure to catalytic reactions.

4. Conclusion

A novel S-scheme composite made of ultra-small copper phosphosuflide nanocrystals coupled with g-C₃N₄ was prepared for photocatalytic CO₂ reduction reaction. The small size (average d = 2.82 nm), PS structure, and the unique interface with P–N bonding of the us-Cu₃P|S/CN composite boosted the photocatalytic CO generation rate to *ca*. 137 µmol g⁻¹ h⁻¹, eight times higher than that of g-C₃N₄. The P–N interfacial bonding between us-Cu₃P|S and g-C₃N₄ acts as an electron transfer channel to facilitate electron migration, leading to enhanced separation efficiency of charge carriers in S-Scheme. The PS structure provides more active sites and contributes to increased conductivity. This is the first application of transition metal phosphosulfides to photocatalytic CO₂ reduction reaction, and provides a significant step forward for the developing of their photocatalytic applications.

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Supporting Information

Supporting Information including TEM, XPS, post-HER XRD, and TRPL fitting results is

available from online version.

Conflict of Interest

The authors declare no conflict of interest.

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