Cu/PCN Metal-Semiconductor Heterojunction by Thermal Reduction for Photoreaction of CO2-Aerated H2O to CH3OH and C2H5OH

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ABSTRACT: g-C3N4-based materials show potential for photoreduction of CO2 to oxygenates but are subjected to fast recombination of photogenerated charge carriers. Here, a novel Cu-dispersive protonated g-C3N4 (PCN) metal-semiconductor (m-s) heterojunction from thermal reduction of a Cu2O/PCN precursor was prepared and characterized using in situ X-ray diffraction, scanning transmission electron microscopy, X-ray photoelectron spectroscopy, ultraviolet–visible (UV–vis) spectra, photoluminescence (PL) spectra, transient photocurrent response, and electrochemical impedance spectroscopy (EIS). The Cu amount in Cu/PCN and the reduction temperature affected the generation of CH3OH and C2H5OH from the photoreaction of CO2-aerated H2O. During calcination of Cu2O/PCN in N2 at 550 °C, Cu2O was completely reduced to Cu with even dispersion, and a m-s heterojunction was obtained. With thermal exfoliation, Cu/PCN showed a specific surface area and layer spacing larger than those of PCN. Cu/PCN-0.5 (12.8 wt % Cu) exhibited a total carbon yield of 25.0 μmol·g−1 under UV–vis irradiation for 4 h, higher than that of Cu0/PCN (13.6 μmol·g−1) and PCN (6.0 μmol·g−1). The selectivity for CH3OH and C2H5OH was 51.42 and 46.14%, respectively. The PL spectra, transient photocurrent response, and EIS characterizations indicated that Cu/PCN heterojunction promotes the separation of electrons and holes and suppresses their recombination. The calculated conduction band position was more negative, which is conducive to the multielectron reactions for CH3OH and C2H5OH generation.

INTRODUCTION

Light-energy-boosted transformation of CO2 and H2O into oxygenates as well as hydrocarbons is desired for sustainable energy exploration of our planet. Semiconductor materials such as TiO2, ZnO, BiVO4, ZnV2O4, g-C3N4, or Cu2O have been studied for methanol generation from the photoreaction of CO2 and H2O. Easily available g-C3N4-based materials have attracted interest due to their unique 2D-layered structure and narrow band gap (~2.7 eV) that respond to visible light energy absorption.1 However, fast recombination of light-excited charge carriers on g-C3N4 is adverse to the photoassisted actions.2 Methods to extend the duration time of photo-generated carriers include exfoliation, metal modification, or semiconductor combination.3 A Au, Ag, or Pd composite g-C3N4 enhanced electron transfer and photoconversion,4–10 although these metals are expensive.

Earth-abundant copper has received attention for photoreduction of CO2 owing to its photocatalytic performance and potential in the formation of C2+ products,11,12 with Cu2+, Cu+, and Cu0 for CO2 adsorption, photoreduction reaction, and charge separation, respectively. Cu2O-decorated g-C3N4 dominated CO production in the gas-phase photocombustion of CO2 through a H2O bubbler due to interfacial charge transfer.13 Cu2O/polymeric carbon nitride assisted CO2 in water to methanol owing to high redox potentials (Ecb = −1.15 eV, Ecpl = 1.65 eV), Z-schematic charge flow, and spatial separation of electrons and holes.14 A g-C3N4-encapsulated Cu2O nanowire as a Z-scheme heterojunction showed enhanced methanol yield and selectivity from the gas-phase photoreaction of CO2 with H2O by facilitating rapid separation of photogenerated electrons and holes.15 Furthermore, under illumination on the (110) face of rhombic dodecahedral Cu2O, Cu+ was converted to Cu0 with coadsorption of CO2 and H2O,16 demonstrating the active site action of Cu0. The synergistic effect of Cu0 and Cu+ on CO2 reduction was reported for Cu/Cu+/TiO217 as Cu+ accelerates charge carrier transfer, whereas Cu acts as the active site for CO2 reduction or as an electron reservoir. AuCu alloy modified ultrathin and porous g-C3N4 nanosheets with strong interaction between metal and g-C3N4 accelerated the migration of photogenerated charges, and the Cu surface promoted the intermediates CO2− and CO for photothermal conversion of CO2 to ethanol.18

Received: March 25, 2022
Accepted: April 18, 2022
Published: May 2, 2022
Composite Cu/ZnO/g-C₃N₄ enhanced methanol generation from CO₂ and H₂O due to suppression of recombination. Cu-based electrocatalyst studies indicated that CO₂ reduction inclines to multicarbon products (C₂⁺) on Cu⁺ sites. This progress reveals distinct impacts of the Cu valence in semiconductor materials on the photoreaction products.

Solution reduction was used for atomically dispersed Cu on ultrathin TiO₂ nanosheets. However, the process is tedious. In situ synthesized Cu/Cu₂O using calcination displays a response extension from visible light to the near-IR region associated with excitation of Cu-localized surface plasmon resonance. Mott–Schottky-type nanohybrids (Cu/NC) with 750 °C condensation increased the Schottky barrier of the Cu—C for CO₂ fixation.

For the above-mentioned process, it is possible that Cu/g-C₃N₄ can be obtained through a thermal reduction method and photoreduction of CO₂ to C₂⁺ products besides methanol.

In this work, g-C₃N₄ and Cu₂O were prepared using thermal polymerization and a solution method, respectively, and the
Cu/PCN m-s heterojunction was obtained using thermal reduction. The resulting Cu/PCN exhibited higher yields toward alcohols. The CH₃OH and C₂H₅OH generation were promoted by a multielectron reaction due to strong interaction on the Cu/PCN m-s heterojunction and a remarkable change in energy level positions, as proven by structural characterizations.

**RESULTS AND DISCUSSION**

**Phases of Synthesized Samples.** From Cu₂O/PCN (protonated g-C₃N₄) precursor and using the thermal reduction process in a N₂ atmosphere, the Cu-dispersive PCN (Cu/PCN) was obtained as depicted in Figure 1a. Cu/PCN-0.5 (12.8 wt % Cu) samples showed X-ray diffraction (XRD) peaks at 2θ of 12.8 and 27.6° (Figure 1b), ascribed to the (100) and (002) crystal planes of g-C₃N₄ (Figure 4).²⁶ The diffraction peaks at 2θ of 36.4, 42.3, 61.3, and 73.5° are ascribed to the (111), (200), (220), and (311) crystal planes of Cu₂O (PDF# 05-0667). As the reduction temperature for Cu₂O/PCN-0.5 was increased from 150 to 300 °C, the peak intensity of Cu₂O decreased. After undergoing 550 °C calcination for 4 h, these peaks disappeared. It was inferred that Cu₂O is reduced to Cu by the reductive PCN, and the resulting Cu species are well-dispersed even in the monolayer. When the nominal Cu amount was greater than 32% (Table S1, calcination temperature 550 °C), the peaks at 2θ of 43.3, 50.4, and 74.1° corresponding to the (111), (200), and (220) crystal planes of Cu were observed (Figure 4), indicating low dispersion of a high Cu composite.

To identify the Cu species, the thermal reduction process of the Cu₂O/PCN-0.5 precursor was traced using in situ XRD, and the results are shown in Figure 2. As the temperature was increased from 50 to 550 °C in N₂ flow, the diffraction patterns were recorded in a temperature interval of 50 °C and in an interval of 30 min when the temperature was kept constant at 550 °C for 4 h. The two diffraction peaks of PCN were observed, indicating that introduction of Cu and calcination temperature do not affect the PCN phase. The shifting of the diffraction peak at 2θ of 27.6° demonstrated the increased layer spacing of PCN associated with thermal exfoliation.⁹ Below 550 °C, the diffraction peak intensity of Cu₂O gradually diminished until it disappeared. Starting from 450 °C, the diffraction peaks of Cu appeared and the intensity increased gradually with the increase in temperature. The diffraction peaks corresponding to the Cu(111) and Cu(200) planes slightly shifted to 2θ of 43.0 and 50.1° owing to the existence of a mixed phase¹⁹,²³ like Cu₂O−Cu. During the constant temperature of 550 °C for 240 min, the diffraction peaks of Cu gradually shrank until they disappeared completely, demonstrating that, on the one hand, Cu₂O is completely reduced to Cu. On the other hand, the resulting Cu is evenly dispersed in the monolayer on PCN. It should be noted that the Cu⁺ and Cu can be tuned with varying calcination temperature and time.

**Photoreaction Activity.** The photoreaction activity of CO₂-aerated H₂O on synthesized samples is shown in Figure 3. The products included CH₃OH, C₂H₅OH, CH₄, CO, and O₂ (O₂ not quantified considering possible reactions with the hole scavenger). From Figure 3a, the Cu amount in Cu/PCN significantly affected the yields of CH₃OH and C₂H₅OH. For Cu/PCN-0.1 with a high Cu amount, the main product was CH₃OH. Cu/PCN-0.2 and Cu/PCN-0.5 showed increased C₂H₅OH product, in particular, with about half-half CH₃OH−C₂H₅OH for Cu/PCN-0.5. From Cu/PCN-0.7 to
Cu/PCN-1.5, as the Cu amount decreased, the CH₃OH yield decreased. As the Cu amount varied (Figure 3b), the CH₄ and CO yields did not show evident change, considering the analysis error in low content. Cu/PCN-1.5 displayed the lowest yields of CO and CH₄ (even less than those on PCN) due to faster recombination of photogenerated carriers (Figure S2). Among all tests on the samples with different Cu amounts, the highest total carbon (TC) yield (25.0 μmol·g⁻¹) was achieved on Cu/PCN-0.5 (Figure 3c), 4.2 times higher than that on PCN, and the H₂ yield reached a maximum (Figure 3d). It was inferred that the promoted TC activity and CH₃OH and C₂H₅OH yields on the Cu-dispersive PCN are associated with the electron reservoir of Cu and Cu active sites. However, there exists an appropriate amount of Cu. Under this circumstance, more photogenerated electron–holes on Cu/PCN might take place in the redox reactions of CO₂-aerated H₂O.

The photoreaction activity of CO₂-aerated H₂O on Cu/PCN-0.5 from different reduction temperatures is shown in Figure 4. As the temperature was increased from 150 to 550 °C, the TC yield for all carbon-containing products increased (Figure 4a). The TC yield on Cu/PCN-550 was 25.0 μmol·g⁻¹, and the CH₃OH and C₂H₅OH selectivity reached 51.4 and 46.1%, respectively. Cu₂O/PCN without calcination promoted generation of C₂H₅OH except for CH₃OH. Cu₂O/PCN-0.5 displayed the lowest yields of CO and CH₄ (even less than those on PCN) due to faster recombination of photogenerated carriers (Figure S2). Among all tests on the samples with different Cu amounts, the highest total carbon (TC) yield (25.0 μmol·g⁻¹) was achieved on Cu/PCN-0.5 (Figure 3c), 4.2 times higher than that on PCN, and the H₂ yield reached a maximum (Figure 3d). It was inferred that the promoted TC activity and CH₃OH and C₂H₅OH yields on the Cu-dispersive PCN are associated with the electron reservoir of Cu and Cu active sites. However, there exists an appropriate amount of Cu. Under this circumstance, more photogenerated electron–holes on Cu/PCN might take place in the redox reactions of CO₂-aerated H₂O.

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ing CH$_3$OH$^{16}$ and a small amount of C$_2$H$_5$OH. This strongly suggested that improvement in photoreaction activity mainly contributes to the formation of Cu. In addition, the CO and CH$_4$ yields exhibited a relatively small change, whereas the H$_2$ yield was higher when the calcination temperature was greater than 300 °C (Figure 4c,d). These results demonstrated that thermal reduction is indispensable for the activity of Cu/PCN toward the photogeneration of CH$_3$OH and C$_2$H$_5$OH. The production of H$_2$ indicated that H$_2$O oxidation simultaneously occurs, accompanying the reduction of CO$_2$.

Using different irradiation reaction times, the photoreaction activity of CO$_2$-aerated H$_2$O on Cu/PCN-0.5 was tested. From Figure 5a, as irradiation time extended from 0.5 to 8 h in separate runs, when the time was within 4 h, the CH$_3$OH and C$_2$H$_5$OH yields were higher. When the time exceeded 6 h, the yields became low, and the activity test for the 6 or 8 h reaction was repeated three times. The selectivity of CH$_3$OH + C$_2$H$_5$OH was greater than 85.7%. By contrast, from Figure 5b, as irradiation time extended, the CO and CH$_4$ yields showed a slight increase, and the H$_2$ yield displayed an evident increase. When the generated amounts of the products were depicted based on per hour (Figure S3), the CH$_3$OH and C$_2$H$_5$OH yields showed a certain decrease after 4 h irradiation reaction, whereas the CO, CH$_4$, and H$_2$ yields remained relatively stable. This may result from second reactions of CH$_3$OH and C$_2$H$_5$OH, for instance, the reverse oxidation induced by high light intensity$^{25}$ or the effect of undesorbed products on active sites.$^{27}$ Although after a 4 h irradiation reaction, the X-ray diffraction peaks of PCN remained unchanged, and the peaks of neither Cu nor copper oxides were observed, suggesting the structural stability of Cu/PCN-0.5 (Figure S4). However, a slight oxidation of Cu is not excluded during the photoreaction.

On the whole, this constructed Cu/PCN of a m-s heterojunction exhibited a higher photoreaction activity toward generation of CH$_3$OH and C$_2$H$_5$OH from CO$_2$-aerated H$_2$O, as compared with g-C$_3$N$_4$-based materials for photo-reduction of CO$_2$ (Table S2).

**Morphology and Dispersion.** PCN from the protonation and exfoliation of g-C$_3$N$_4$ showed the layer-stacking structure (Figure 6a). Synthetic Cu$_2$O exhibited a uniform rhombic dodecahedral structure with even dispersion and no aggregation (Figure 6b). From Cu$_2$O/PCN-0.5 before thermal reduction (Figure 6c), Cu$_2$O monospherical particles were dispersed on the PCN surface. For Cu/PCN-0.5 undergoing calcination at 550 °C, the PCN surface was further exfoliated into porous layers due to thermal circumstances (Figure 6d). Meanwhile, the dispersed Cu$_2$O particles were reduced to Cu spreading into PCN layers. The above structure of Cu nanoparticles (NPs) on the porous layered surface of PCN were further observed (Figure 6e,f), demonstrating the formation of the Cu/PCN m-s heterojunction.

**Figure 6.** SEM images for (a) PCN, (b) Cu$_2$O, (c) Cu$_2$O/PCN-0.5, and (d) Cu/PCN-0.5. (e,f) HRTEM images for Cu/PCN-0.5.

**Figure 7.** HAADF images, Cu, N, and C mapping, and SAED of Cu/PCN-0.5.
A high-angle annular dark-field (HAADF) image (Figure 7) demonstrated the sparse and porous surface of Cu/PCN-0.5. Mapping results revealed the uniform distribution of Cu, N, and C elements in Cu/PCN-0.5. In addition, the selected area electron diffraction (SAED) rings of Cu(111), Cu(200), and PCN(002) proved the existence of Cu crystals, which was not observed in the XRD phase analysis.

Synthesized samples showed type IV N$_2$ adsorption−desorption isotherms (Figure S5). The adsorption volume increased from $P/P_0 > 0.8$ due to the capillary coalescence. The H3-type hysteresis loop indicated the irregular fractured pore. Cu/PCN-0.5 showed higher specific surface area and pore volume than PCN due to a larger hysteresis loop and adsorption volume. Moreover, Cu/PCN-0.5 had more 5−50 nm mesopores than PCN. The increase in the specific surface area/pore volume and even dispersion of Cu on the PCN surface (Figures 6 and 7) promote the CO$_2$ adsorption and multielectron photoreactions for generation of CH$_3$OH and C$_2$H$_5$OH.

The surface elemental composition and valence state were analyzed using XPS. In the full spectrum (Figure S6), the electron binding energy peaks of Cu 2p, N 1s, and C 1s were observed. As shown in Figure 8a, the binding energies of 287.85 and 284.4 eV are attributed to the C atoms in N=C−N and surface C−C, respectively, whereas those of 400.82, 399.17, and 398.43 eV are attributed to the bridging N atoms in N−H, N(−C)$_3$, and C=N−C in PCN, respectively (Figure 8b). The shift of N 1s and C 1s by Cu/PCN-0.5 proved a strong interaction between Cu and the PCN surface. Additionally, the binding energies of 952.08 and 932.38 eV in the spectra are ascribed to Cu 2p1/2 and Cu 2p3/2 of Cu, respectively (Figure 8c).

**Photoelectric Properties.** Photoluminescence (PL) spectroscopy is one of effective methods to estimate the recombination rate of photogenerated carriers. A lower PL intensity implies longer lifetime of photogenerated electrons−holes, favorable for photocatalytic reactions. From Figure 9a, Cu/PCN-0.5 presented similar PL spectra with PCN. Its PL intensity, however, was far lower than that of PCN, which showed a broad absorption peak near 472 nm. The substantial decrease in the peak intensity indicated that recombination of carriers was greatly suppressed. The Cu/PCN m-s heterojunction possesses performances for rapid migration of photogenerated electrons and for retarding the charge recombination.

From the PL spectra of Cu/PCN-x (Figure S2), Cu/PCN-1.5 showed the strongest peak, whereas Cu/PCN-0.1 had the weakest one, suggesting the difference of photogenerated electron−hole recombination rate on Cu/PCN with varied Cu amount. This proved that Cu can effectively capture the photogenerated electrons on PCN and promote the charge separation. However, Cu/PCN-0.5 exhibited the best photocatalytic activity, implying that PL is not the absolute indicator for catalytic performance. The PL decay properties of PCN
with Cu introduction were further revealed using time-resolved photoluminescence (TRPL) spectra. The Origin ExpDec2 basic function ($y = y_0 + A_1 e^{(-x/\tau_1)} + A_2 e^{(-x/\tau_2)}$) was employed to fit the average decay life ($\tau_{ave} = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2)$) with fit convergence matching $R^2 \geq 0.99$. From Figure 9b, the PL average lifetime of Cu/PCN-0.5 increased to 4.75 from 3.95 ns of PCN. A longer electron−hole lifetime favors the effective charge separation.31 This can be attributed to the even dispersion of Cu on the PCN surface, which effectively extracts photogenerated electrons. As a result, the Cu/PCN m-s heterojunction interface improves the activity of photocatalytic reduction of CO2 in H2O. Cu/PCN-0.5 exhibits a CH3OH yield of 12.85 $\mu$mol·g$^{-1}$ during 4 h irradiation and was 2.47 times that of PCN (5.19 $\mu$mol·g$^{-1}$) (Figure 3). Although this change in the TRPL decay time in the interface is only a few nanoseconds, it affects the photoreaction activity significantly.

A stronger photocurrent represents better separation and transfer of photogenerated electrons and holes. The multiple cycle tests were carried out through the on/off switch of a lamp. As indicated in Figure 9c, the photocurrent signal was detected for PCN and Cu/PCN-0.5 under irradiation. The enhanced photocurrent density signal of Cu/PCN-0.5 can be attributed to higher electron extraction efficiency of Cu on the Cu-PCN interface, which accelerates the transport of photogenerated electrons and promotes the CO2 reduction reaction.

The semicircle radius of electrochemical impedance spectroscopy relates to the impedance. A smaller radius indicates lower resistance for the charge transfer. In Figure 9d, as the impedance semicircle radius of Cu/PCN-0.5 in the Nyquist curve became smaller, the charge transfer resistance in the interface region is lower. As a result, the Cu NPs on PCN as an electron reservoir lower the charge transfer resistance and provide more electrons for multielectron reduction reaction.

From the UV−vis diffuse reflectance absorption spectra (Figure S7), PCN with an absorption edge at 470 nm showed the UV and partially visible absorption range. The visible absorption properties of Cu/PCN-x were significantly improved. The visible absorption intensity increased with the Cu amount, and the sample color became gradually darker (Figure S6, inset). The absorption peak at 760 nm, ascribed to the Schottky effect, indicated the formation of the m-s heterojunction between Cu and PCN. The Mott−Schottky heterojunction interface can accelerate charge transfer, improving the catalytic activity.32 The calculated band gaps of PCN and Cu/PCN-0.5 were 2.71 and 2.11 eV, respectively, using the Tauc equation, $(\alpha h\nu)^{1/n} = A(nh\nu − E_g)$ (Figure S8). As shown in Figure S9, the valence band (VB) positions were measured by the XPS valence band spectra. The VB positions of PCN and Cu/PCN-0.5 were 1.78 and 0.58 eV, respectively, whereas their conduction band (CB) positions were −0.99 and −1.53 eV, calculated from $E_g = E_{VB} − E_{CB}$, which matched the

Figure 9. (a) PL spectra (inset for enlarged the y axis), (b) time-resolved PL spectra, (c) photocurrent response curves, and (d) Nyquist plots of PCN and Cu/PCN-0.5.
reaction potentials of $E^{\theta}_{\text{CO}_2/\text{CH}_3\text{OH}}$ (−0.38 V), $E^{\theta}_{\text{CO}_2/\text{CH}_3\text{OH}}$ (−0.33 V), and $E^{\theta}_{\text{H}_2\text{O}/\text{H}_2}$ (−0.41 V).\(^9\) As a result, more photoexcited electrons are beneficial to the 6e/12e reactions for CH$_3$OH/C$_2$H$_5$OH.

# MECHANISM

The kinetics process of CO$_2$ photoreduction includes generation of carriers, transfer separation of electrons, and adsorption activation of CO$_2$/H$_2$O. The e$^-$ and h$^+$ are involved in the redox reactions to produce CH$_3$OH, CO, CH$_4$, H$_2$, and H$^+$. Adsorption activation of CO$_2$/H$_2$O. The excited electrons are beneficial to the 6e/12e reactions for alcohol product formation.

The photoreaction pathway was proposed on the basis of the Schottky barrier mechanism on the cocatalyst metal–semiconductor interface and the characterization results. As shown in Figure 10, the well-dispersed Cu NPs on the PCN surface form the Cu-PCN m-s heterojunction. Under irradiation, electrons transit from the VB to the CB of PCN, and some of the photogenerated electrons are further transferred through the Schottky barrier from the CB of PCN to the Cu NPs’ surface. The h$^+$ left on PCN first oxidizes H$_2$O to •OH and H$. ^{36}$ •OH, e$, ^{36}$ and h$^+$ are the active species,\(^{36}\) which are indispensable for the photoreaction of CO$_2$ and H$_2$O on Cu/PCN-0.5, as confirmed by the active species capture experiments (Figure S10). Further activation of the intermediates and the formation of C–C coupling can be via the carbene ($^*\text{CO}$) or formaldehyde ($^*\text{HOCO}$) mechanisms as observed by in situ characterization.\(^{37,38}\) The h$^+$ and e$^-$ participate in the subsequent reactions for alcohol production.

The aforementioned photocurrent response curves, EIS, and PL spectra confirm the separation, transfer of carriers and suppression of their recombination on Cu/PCN. Change in the TRPL decay time proves the dynamic behavior of the charge carriers.\(^{39}\) CO$_2$-saturated H$_2$O solution contains H$^+$, CO$_2^-$, and H$_2$CO$_3$ reactive species (when the pH is about 7),\(^{33}\) which is conducive to the product formation via the multielectron reactions involving e$^-$ and h$. ^{36}$ Additionally, the VB position (0.58 eV) and the CB position (−1.53 eV) of Cu/PCN-0.5 match the redox potentials of CO$_2$-saturated H$_2$O and have more electrons for the redox reactions.\(^{13,40,41}\)

# EXPERIMENTAL SECTION

## Materials

Melamine (99%), HNO$_3$ (65%), oleic acid (85–95%), Cu(NO$_3$)$_2$·3H$_2$O (99%), NaOH, and cyclohexane (99.5%) were purchased from Macklin Co. and used without further treatment. Deionized water was used for all experiments.

## Catalyst Preparation

g-C$_3$N$_4$ was obtained through thermal polymerization. An appropriate amount of melamine powder in a corundum crucible was calcined at 550 °C for 4 h in a muffle furnace. After being cooled, the residue was ground in a marble mortar and yellow powder of g-C$_3$N$_4$ was obtained.

Protonated g-C$_3$N$_4$ was protonated and exfoliated. g-C$_3$N$_4$ and aqueous nitric acid solution (0.1 mol/L) were mixed in a ratio of 1:50 (g/mL), stirred vigorously for 2 h, sonicated for 2 h, stirred for another 2 h, centrifuged at 7000 rpm for 5 min, washed with deionized water and ethanol, and dried at 80 °C overnight to obtain the light-yellow powder of PCN.

To obtain Cu$_2$O, 40 mL of an aqueous solution of copper nitrate (0.025 mol/L) was placed in a three-necked flask with oil bath heating. Twenty-four milliliters of alcohol solution of oleic acid (oleic acid/ethanol: 1/5) was added and stirred vigorously for 0.5 h. Next, 8 mL of NaOH solution (1 mol/L) and 30 mL of glucose solution (0.02 mol/L) were dropped into the flask and stirred for 1 h to form an orange-red solution followed by centrifugation, washing using deionized water, cyclohexane, and ethanol, and then vacuum-dried at 80 °C overnight to obtain Cu$_2$O as a brick-red powder.

To obtain Cu/PCN-x, 0.1, 0.2, 0.5, 0.7, 1.0, or 1.5 g of PCN was added to 40 mL of Cu(NO$_3$)$_2$ solution (0.001 mol/L), and the same procedure as the Cu$_2$O preparation was used to obtain Cu$_2$O/PCN powder followed by calcination in a N$_2$ flow (20 mL/min) at 550 °C for 4 h and denoted as Cu/PCN-0.1, Cu/PCN-0.2, Cu/PCN-0.5, Cu/PCN-0.7, Cu/PCN-1.0, and Cu/PCN-1.5, respectively. The Cu amount in Cu/PCN is shown in Table S1. The Cu/PCN-0.5 sample calcined at 150, 300, or 550 °C for 4 h is denoted as Cu/PCN-150, Cu/PCN-300, or Cu/PCN-550, respectively.

## Characterization

X-ray diffraction was conducted on a Rigaku XRD D8 with Cu Kα at 40 kV/40 mA. In situ XRD was carried out on Rigaku Smart Lab. A 50 mg sample was loaded into an in situ cell. In a N$_2$ flow (10 mL/min) of normal pressure, as the sample was heated from 25 to 550 °C at 10 °C/min, the XRD pattern was recorded at an interval of 50 °C for 30 min hold and an interval of 30 min at 550 °C for 4 h. The specific surface area was calculated by means of N$_2$ adsorption on a JW-BK132F instrument. Microscopic morphology was observed on a scanning electron microscope (Zeiss Merlin Compact/Oxford x-max) at 520 kV using the

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Form the Cu-PCN m-s heterojunction. Under irradiation, electrons transit from the VB to the CB of PCN, and some of the photogenerated electrons are further transferred through the Schottky barrier from the CB of PCN to the Cu NPs’ surface. The h$^+$ left on PCN first oxidizes H$_2$O to •OH and H$. ^{36}$ •OH, e$, ^{36}$ and h$^+$ are the active species,\(^{36}\) which are indispensable for the photoreaction of CO$_2$ and H$_2$O on Cu/PCN-0.5, as confirmed by the active species capture experiments (Figure S10). Further activation of the intermediates and the formation of C–C coupling can be via the carbene ($^*\text{CO}$) or formaldehyde ($^*\text{HOCO}$) mechanisms as observed by in situ characterization.\(^{37,38}\) The h$^+$ and e$^-$ participate in the subsequent reactions for alcohol product formation.

The aforementioned photocurrent response curves, EIS, and PL spectra confirm the separation, transfer of carriers and suppression of their recombination on Cu/PCN. Change in the TRPL decay time proves the dynamic behavior of the charge carriers.\(^{39}\) CO$_2$-saturated H$_2$O solution contains H$^+$, CO$_2^-$, and H$_2$CO$_3$ reactive species (when the pH is about 7),\(^{33}\) which is conducive to the product formation via the multielectron reactions involving e$^-$ and h$. ^{36}$ Additionally, the VB position (0.58 eV) and the CB position (−1.53 eV) of Cu/PCN-0.5 match the redox potentials of CO$_2$-saturated H$_2$O and have more electrons for the redox reactions.\(^{13,40,41}\)

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**Figure 10.** Electron transfer on Cu/PCN interface (pH of the reaction solution was ~7, near pH 7 for NHE).
gold-sprayed sample and on a field emission transmission electron microscope (FEI Talos F200i). The surface composition of the sample was analyzed on a Thermo Scientific K-Alpha X-ray photoelectron spectrometer, Al Kα, with C 1s (284.6 eV) as the background correction.

The photoluminescence spectra were measured on an Edinburgh FLS1000 steady-state/transient fluorescence spectrometer at an excitation wavelength of 325 nm. The diffuse reflectance spectra were measured on a Shimadzu UV-3600 UV–vis–NIR spectrophotometer. The band gap energy ($E_g$) was calculated according to the Kubelka–Munk equation $(a h \nu)^{1/2} = A(h \nu - E_g)$, where $a$ is the absorption coefficient and $n$ is 1/2 or 2. Specifically, $E_g$ was obtained from the intersection of the starting curve with the $h \nu$ axis. The transient photocurrent response and photochemical impedance measurement for the Cu/PCN catalyst. To understand the reactive species in the reaction process, the active species capture experiments on Cu/PCN-0.5 were carried out under the same reaction conditions.

### Supporting Information

The Supporting Information includes XRD, pore distribution, PL spectra, diffuse reflectance UV–vis spectra, and XPS (PDF). For more details, see [this link](https://pubs.acs.org/doi/10.1021/acsomega.2c01827).

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**Notes**

The authors declare no competing financial interest.

**Acknowledgments**

The authors acknowledge financial support from the National Natural Science Fund of China (21965028) and the East-West cooperation project of Ningxia Key R&D Plan (2017BY063).
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