Conjugated Acetylenic Polymers Grafted Cuprous Oxide as an Efficient Z-Scheme Heterojunction for Photoelectrochemical Water Reduction

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As attractive materials for photoelectrochemical hydrogen evolution reaction (PEC HER), conjugated polymers (e.g., conjugated acetylenic polymers [CAPs]) still show poor PEC HER performance due to the associated serious recombination of photogenerated electrons and holes. Herein, taking advantage of the in situ conversion of nanocopper into Cu2O on copper cellulose paper during catalyzing of the Glaser coupling reaction, a general strategy for the construction of a CAPs/Cu2O Z-scheme heterojunction for PEC water reduction is demonstrated. The as-fabricated poly[2,5-diethynylthieno[3,2-b]thiophene] (pDET)/Cu2O Z-scheme heterojunction exhibits a carrier separation efficiency of 16.1% at 0.3 V versus reversible hydrogen electrode (RHE), which is 6.7 and 1.4-times higher respectively than those for pDET and Cu2O under AM 1.5G irradiation (100 mW cm−2) in the 0.1 m Na2SO4 aqueous solution. Consequently, the photocurrent of the pDET/Cu2O Z-scheme heterojunction reaches =520 µA cm−2 at 0.3 V versus RHE, which is much higher than pDET (=80 µA cm−2), Cu2O (=100 µA cm−2), and the state-of-the-art cocatalyst-free organic or organic-semiconductor-based heterojunctions/homojunctions photocathodes (1–370 µA cm−2). This work advances the design of polymer-based Z-scheme heterojunctions and high-performance organic photoelectrodes.

Photoelectrochemical (PEC) hydrogen production is an attractive and sustainable technique to directly convert intermittent solar energy into storable hydrogen fuel.[1,2] In the last few years, numerous environmentally friendly, inexpensive, and efficient semiconductor photoelectrodes have been developed.[3–6] Up to now, the field of PEC water splitting is dominated by inorganic semiconductors consisting of earth abundant elements (e.g., silicon,[7–12] metal oxides,[13–16] metal sulfides,[17,18] dichalcogenide,[19] etc.). However, the high cost and poor stability of noble metal (e.g., Pt) as cocatalysts seriously restrict the practical applications of inorganic semiconductors for the PEC hydrogen evolution reaction (HER). Compared with traditional inorganic semiconductors, organic semiconductors (e.g., graphitic carbon nitride [g-C3N4 or polyheptazine],[20–23] polythiophene,[24,25] conjugated covalent organic frameworks [COFs],[26] conjugated acetylenic polymers [CAPs],[27–29]) have attracted increasing attentions benefitting from their tunable bandgaps, engineered band edge positions, and molecular-level desirable active centers.[6] However, the PEC HER performance of current organic photocathodes falls far behind inorganic counterparts mainly due to their severe recombination of photoinduced holes and electrons.

Recently, diverse strategies have been explored for promoting the charge separation of organic semiconductors, mainly focusing on the heterojunction or homojunction...
Among them, the formation of a type-II heterojunction, attributable to the effective separation of photoinduced electron–hole pairs through the band bending between two semiconductors, is one of the most facile ways for enhancing the PEC performance (Figure 1a). Unfortunately, for the type-II heterojunction, the reduction and oxidation reactions occur under lower potentials, respectively, resulting in a significantly reduced redox activity. In addition, due to electrostatic repulsion among electron–electron or hole–hole, it is difficult for the migration of photoinduced electrons/holes between two semiconductors. Therefore, the separation efficiency of photoinduced electrons and holes is still inferior even in the conjugated-polymer-based type-II heterojunctions or homojunctions with continuous type-II alignments (<2%).

Compared with type-II heterojunction, the Z-scheme heterojunction has a similar band structure but different charge-carrier migration mechanism (charge-carrier migration pathway resembles the letter “Z”). The Z-scheme heterojunction can not only achieve complementary light absorption and efficient separation of photogenerated carriers, but also reserve their strong photo redox properties for catalytic reactions (Figure 1b). Moreover, the charge-carrier migration in the Z-scheme heterojunction is physically more feasible than that for the type-II heterojunction due to the electrostatic attraction between the electron and hole. However, owing to the embarrassment in constructions of the “Z” like charge-carrier migration pathway between two organic semiconductors or one organic and one inorganic semiconductors, the fabrication of organic-semiconductor-based Z-scheme heterojunction remains unexplored for the PEC water reduction.

In this work, we report a general approach for the one-step fabrication of CAPs/Cu$_2$O Z-scheme heterojunction on Cu cellulose paper (CP) for the first time. The Cu$_2$O in such Z-scheme heterojunction is converted from the nanocopper which can be readily oxidized during the catalytic Glaser-coupling of acetylenic monomers. The charge carriers separation efficiency measurement reveals that the as-synthesized poly(2,5-diethynylthiophene) (pDET)/Cu$_2$O Z-scheme heterojunction (noted as pDET/Cu$_2$O Z-scheme heterojunction) effectively boosts the separation of photoinduced electrons and holes in contrast to either pure pDET or Cu$_2$O, which is attributed to the large energy difference between VB of pDET and CB of Cu$_2$O. As a result, in 0.1 M Na$_2$SO$_4$ aqueous solution, the pDET/Cu$_2$O Z-scheme heterojunction exhibits a substantially enhanced photocurrent of 520 µA cm$^{-2}$ at 0.3 V versus RHE, which is ~6.5 and ~5.2 times higher than those for pure pDET and Cu$_2$O, respectively, as well as superior to the state-of-the-art cocatalyst-free organic semiconductors or organic-semiconductor-based heterojunctions photocathodes (1–370 µA cm$^{-2}$).

The CP was first pretreated by chlorauric acid solution (2 mg mL$^{-1}$) for 2 h and reduced in sodium borohydride solution to create the nucleation centers for Cu. Then Cu CP was prepared by seed-mediated growth method in an aqueous solution containing copper sulfate (30 mg mL$^{-1}$), sodium hydroxide (40 mg mL$^{-1}$), potassium sodium tartrate (120 mg mL$^{-1}$), and formaldehyde (100 µL mL$^{-1}$) for 5 h at room temperature. After the metallic Cu was deposited on the cellulose

![Figure 1](https://www.advmat.dewww.advancedsciencenews.com/2002486/202002032) (2 of 7) © 2020 The Authors. Published by Wiley-VCH GmbH

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**Figure 1.** a,b) Band alignment in type II (a) and Z-scheme (b) heterojunctions. A and B are two different semiconductors. CB, conduction band; VB, valence band.
Considering the band levels of pDET (conduction band level \(E_c\): \(-3.06\) eV; valence band level \(E_v\): \(-5.23\) eV)\(^{[29]}\) and Cu\(_2\)O (\(E_c\): \(-3.2\) eV; \(E_v\): \(-5.3\) eV)\(^{[5]}\) as well as the fact that both pDET and Cu\(_2\)O are grown on the copper layer on the Cu CP, the metallic copper in the pDET/Cu CP can function as mediate to migrate the photoinduced electron from the CB of Cu\(_2\)O to the VB of pDET, thus realizing the construction of Z-scheme heterojunction between pDET and Cu\(_2\)O (pDET/Cu\(_2\)O Z-scheme heterojunction).

The chemical composition and bonding information of pDET/Cu\(_2\)O Z-scheme heterojunction are analyzed using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The characteristic Raman peak and XPS binding energy for C≡C triple bonds of pDET/Cu foil and pDET/Cu\(_2\)O Z-scheme
heterojunction are located at 1910/2185 cm\(^{-1}\) and 284.0 eV (Figures S9–S11, Supporting Information), respectively.\[27–29,42,43\] However, compared with the Raman spectrum of pDET/Cu foil, the decreased intensity at 2185 cm\(^{-1}\) and the increased intensity at 1910 cm\(^{-1}\) of pDET/Cu\(_2\)O Z-scheme heterojunction arise from the strong interaction between Cu substrate and C≡C triple bonds in the pDET/Cu\(_2\)O Z-scheme heterojunction.\[44,45\] Meanwhile, to clarify the electron transfer direction between pDET and Cu\(_2\)O experimentally and whether it complies with the Z-scheme or type-II heterojunction pathway, high-resolution in situ XPS characterizations for Cu\(_{2p}\) of pDET/Cu CP were conducted. The positive shift binding energy (=0.1 eV) of Cu\(_{2p}\) under UV-light irradiation was due to the electron density reduction of Cu\(_2\)O.\[46–48\] These results showed the photo-generated electrons migration from Cu\(_2\)O to pDET, evidencing its Z-scheme pathway (Figure S12, Supporting Information).

In order to investigate the photoinduced electron–hole separation behavior in pDET/Cu\(_2\)O Z-scheme heterojunction, the carrier separation efficiency of photoelectrodes was evaluated according to the following equation:\[28,29,49\]
\[
\eta_{\text{sep}} \times \eta_{\text{cat}} \times \eta_{\text{ph}} = \frac{j_{\text{ph}}}{j_{\text{abs}}} = \eta_{\text{sep}} \times \eta_{\text{cat}}
\]
\(j_{\text{ph}}\): total photocurrent density; \(j_{\text{abs}}\): photon absorption rate expressed as current density; \(\eta_{\text{sep}}\): carrier separation efficiency; \(\eta_{\text{cat}}\): catalytic efficiency for water reduction.\[28,29,49\] At 0.3 V versus RHE, the carrier-separation efficiency of pDET/Cu\(_2\)O Z-scheme heterojunction was about 16.1% (Figure 3a), which was 6.7 and 1.4 times higher than 2.4% for pDET on Cu foil (pDET/Cu foil) and 11.6% for Cu\(_2\)O on the Cu foil (Cu\(_2\)O/Cu foil, Figures S13,S14, Supporting Information), respectively. These results evidence that the Z-scheme heterojunction of pDET and Cu\(_2\)O significantly improves its separation efficiency of photoinduced electrons and holes, which stand in contrast with pure pDET and Cu\(_2\)O.

The PEC measurements of pDET/Cu\(_2\)O Z-scheme heterojunction, pDET/Cu foil, and Cu\(_2\)O/Cu foil photocathodes were subsequently carried out in a 0.1 M Na\(_2\)SO\(_4\) aqueous solution (pH 6.8) to study the influence of the enhanced separation of photoinduced charge carriers on PEC HER performance. As revealed by the linear sweep voltammetry under the standard solar radiation (AM 1.5G, 100 mW cm\(^{-2}\)), pDET/Cu foil, Cu\(_2\)O/Cu foil, and pDET/Cu\(_2\)O Z-scheme heterojunction photocathode delivered obvious photocurrent responses to light on/off switching. By contrast, pure Cu CP did not show any PEC response (Figure 3b; Figures S15,S16, Supporting Information). As presented in Figure 2a,b, pDET/Cu foil, and Cu\(_2\)O/Cu foil exhibited photocurrents of \(\approx 80\) and 100 \(\mu\)A cm\(^{-2}\) at 0.3 V versus RHE under solar irradiation, respectively. Remarkably, the photocurrent of pDET/Cu\(_2\)O Z-scheme heterojunction reached 520 \(\mu\)A cm\(^{-2}\), which is 6.5 and 5.2 times higher than those of pDET/Cu foil and Cu\(_2\)O/Cu foil, respectively (Figure 3c). It should be noted that the photocurrent of pDET/Cu\(_2\)O Z-scheme heterojunction exceeded those of thus-far reported cocatalyst-free organic photocathodes and organic-semiconductor-based heterojunctions/homojunctions photocathodes (1–370 \(\mu\)A cm\(^{-2}\), Table S1, Supporting Information)\[20–24,26,28,31\] as well as many cocatalyst-free inorganic photocathodes, for example, Cu\(_2\)O (\(\approx 200\) \(\mu\)A cm\(^{-2}\)).\[15\]

![Image](image.png)

**Figure 3.** a) Carrier-separation efficiency (\(\eta_{\text{sep}}\)) of pDEB/Cu foil, Cu\(_2\)O/Cu foil, and pDET/Cu\(_2\)O Z-scheme heterojunction as a function of the applied potential. b) Photocurrent-potential plots for the pDET, Cu\(_2\)O, and pDET/Cu\(_2\)O Z-scheme heterojunction photocathodes. c) pDET, Cu\(_2\)O, and pDET/Cu\(_2\)O Z-scheme heterojunction photocathodes at 0.3 V versus RHE (the dark currents in (c) have been deducted). d) Comparison with the state-of-the-art cocatalyst-free organic and inorganic photocathodes (photocurrents at 0.3 V vs RHE; IPCE values at 520 nm).
NiO ($\approx 30 \mu$A cm$^{-2}$), CuInS$_2$ ($\approx 30 \mu$A cm$^{-2}$), and WSe$_2$ ($\approx 300 \mu$A cm$^{-2}$). As another important parameter to evaluate the intrinsic PEC performance of photoelectrode, the incident-photon-to-current efficiency (IPCE) was measured as well. As shown in Figure S17, Supporting Information, the pDET, Cu$_2$O, and pDET/Cu$_2$O Z-scheme heterojunction achieved the maximum IPCE values at wavelengths of 520 nm. In particular, the peak IPCE value of pDET/Cu$_2$O Z-scheme heterojunction was up to 22.1%, which was much higher than 77% for pDET and 6.3% for Cu$_2$O (Figure 2d) and those of the state-of-the-art cocatalyst-free organic photocathodes and organic-semiconductor-based heterojunctions/homojunction photocathodes, for example, g-C$_3$N$_4$ ($\approx 0.3–0.6$%)[22,23] BDT-ETTA COF ($\approx 0.6$%)[26] CAPs ($\approx 1.1–12.1$%),[27,29] pDEB gradient homojunction (2.9%),[28] and many inorganic photocathodes including Cu$_2$O ($\approx 10.0$%),[15] NiO ($\approx 1.5$%),[16] and WSe$_2$ ($\approx 0.2$%)[19] (Figure 3d). In addition, given that the CP has good flexibility, the pDET/Cu$_2$O Z-scheme heterojunction photocathode is also flexible and exhibits great potential as flexible electrode (Figure S18, Supporting Information).

The long-term PEC HER stability of pDET/Cu$_2$O Z-scheme heterojunction was further evaluated at 0 V versus RHE (Figures S19–S23, Supporting Information). The gaseous product generated from the pDET/Cu$_2$O Z-scheme heterojunction was synchronously analyzed using a gas chromatograph (GC). Experimentally detected H$_2$ amount reached $\approx 25 \mu$mol with a Faradic efficiency of $\approx 90$% after 2 h PEC reaction. Under the solar light irradiation, the photocurrent ($\approx 600 \mu$A cm$^{-2}$) of pDET/Cu$_2$O Z-scheme heterojunction showed no decrease (Figure S19, Supporting Information). After the PEC HER stability test, the morphology and chemical composition of pDET/Cu$_2$O Z-scheme heterojunction were examined. Obviously, scanning electron microscopy (SEM) images revealed that the sheet-like morphology of pDET was well maintained (Figure S20, Supporting Information). The Raman spectra and XRD pattern further revealed that no changes of chemical composition and bonding information of pDET/Cu$_2$O Z-scheme heterojunction occurred during the PEC HER process (Figures S21, S22, Supporting Information), confirming the excellent electrochemical stability of pDET/Cu$_2$O Z-scheme heterojunction photocathode against the photocorrosion.[50–52]

To unveil the generality of the synthesis approach to construct the CAPs/Cu$_2$O Z-scheme heterojunction, three other

![Figure 4. a) Schematic representation of band positions of pDEB, pDEN, pDTT, pDET, and Cu$_2$O.[5,29] b) Band alignment in CAP/Cu$_2$O Z-scheme heterojunctions. Metallic Cu in the CP work as the mediate to migrate the photoinduced electron from the CB of Cu$_2$O to the VB of CAP. c) The relationship of energy difference between $E_v$ of CAP and $E_c$ of Cu$_2$O ($\Delta E$) and the PEC performance of CAP/Cu$_2$O Z-scheme heterojunction.](advmat.de)
CAPs (poly[1,4-diethynylbenzene] [pDEB], poly[2,6-diethynyl-naphthalene] [pDEN], and poly[2,5-diethynylthiophene] [pDTT]) were also synthesized on the Cu CP using the Cu-mediated Glaser coupling method (Figures S24–S26, Supporting Information). The similar nanosheet-like morphologies of pDEB, pDEN, and pDTT were generated on both Cu foil and Cu CP (Figures S27–S32, Supporting Information). XRD and Raman measurements demonstrated the successful conversion of nanocopper to Cu₂O and the strong interaction between C≡C triple bonds and Cu substrate in Cu CP for all samples (Figures S33–S38, Supporting Information). We found that the PEC performance of these CAPs/Cu₂O heterojunctions depended significantly on the band structure of CAPs, especially for the energy difference between E_v of CAP and E_c of Cu₂O (∆E). As shown in the Figure 4 and Figures S39–S41, Supporting Information, the larger ∆E results in a larger electrostatic attraction between the photoinduced electrons from Cu₂O and photoinduced holes from CAPs. As presented above, for the pDET/Cu₂O Z-scheme heterojunction, the ∆E is ≈0.2 eV and its photocurrent at 0.3 V versus RHE can reach 520 μA cm⁻² with an ≈75-fold enhancement in comparison with pure pDET. Upon decreasing ∆E down to ≈1.9 eV for pDTT and ≈1.4 eV for pDET, their photocurrents at 0.3 V versus RHE are 270 and 110 μA cm⁻² with an ≈4.5- and ≈2.9-fold enhancement with respect to the pristine polymers, respectively. However, for pDEN/Cu₂O heterostructure, the ∆E further decreases to ≈0.4 eV, and no obvious promotion of photocurrent compared with pure pDEN was observed. Thereby, our results highlight the generality of one-step integration of the Z-scheme CAPs/Cu₂O heterojunctions on Cu CP.

In summary, we have presented a novel strategy for the construction of organic/inorganic Z-scheme heterojunction based on the in situ conversion of nanocopper into Cu₂O during the growth of CAPs. The PEC HER performance of the achieved CAPs/Cu₂O heterojunction depends on the energy difference between E_v of CAPs and E_c of Cu₂O. The photoinduced electrons and holes in pDET/Cu₂O Z-scheme heterojunction are more efficiently separated in comparison with pure pDET and Cu₂O. As a result, the pDET/Cu₂O Z-scheme heterojunction photocathode presents a benchmark photocurrent density (≈520 μA cm⁻²) that substantially exceeds the reported organic semiconductors and organic-semiconductor-based heterojunctions or homojunctions (1–370 μA cm⁻²). Therefore, our design strategy of CAPs/Cu₂O Z-scheme heterojunctions sheds light on exploring high-performance organic photoelectrodes, which holds promising applications in the fields of solar-to-fuel conversions such as water splitting, CO₂ reduction, N₂ reduction, and artificial photosynthesis.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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