Cu$_2$O/ZnO p–n Junction Decorated with NiO$_x$ as a Protective Layer and Cocatalyst for Enhanced Photoelectrochemical Water Splitting

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**ABSTRACT:** Cuprous oxide (Cu$_2$O) has attracted much interest as a photocathode for photoelectrochemical (PEC) water splitting because of its elemental abundance and the favorable band gap, but its poor stability in aqueous solutions hinders the practical PEC application. Compared to the mostly used TiO$_2$ and noble metal cocatalysts for coating the Cu$_2$O photocathode, this work demonstrates a strategy to fabricate a noble metal-free photocathode. We construct a Cu$_2$O/ZnO p–n junction photocathode decorated with the NiO$_x$ layer as both the protective layer and the hydrogen evolution reaction (HER) cocatalyst. The NiO$_x$ cocatalyst exhibits a small Tafel slope of 35.9 mV/dec and a very low overpotential of 115 mV to drive a current of 10 mA/cm$^2$, which are very close to the HER activity of the noble metal platinum. With decorated NiO$_x$, the Cu$_2$O/ZnO/NiO$_x$ photocathode exhibits significantly improved stability and photocurrent density with a Faradaic efficiency of $95\pm4\%$, distinctly outperforming the Cu$_2$O, Cu$_2$O/ZnO, and Cu$_2$O/ZnO/TiO$_2$ photocathodes. Moreover, electrochemical impedance analysis evidenced that NiO$_x$ as a cocatalyst also facilitates the transfer of photogenerated electrons across the electrode/electrolyte interface for water reduction. This work demonstrates that NiO$_x$ is not only a stable protective layer against corrosion but also a highly active H$_2$ evolution cocatalyst. These findings provide new insights for the design of noble metal-free photocathodes toward solar fuel development.

**KEYWORDS:** cuprous oxide, nickel oxide, water reduction cocatalyst, p–n junction, photoelectrochemical water splitting

1. INTRODUCTION

Photoelectrochemical (PEC) water splitting represents an attractive method to capture and store the immense energy of sunlight in the form of hydrogen, a clean chemical fuel.$^{1-5}$ To accomplish efficient solar energy conversion in the PEC water splitting cell, the semiconductor photoelectrode should meet the essential criteria including efficient sunlight absorption and carrier separation, high water splitting activity, and long-term stability.$^{6-10}$ In the past decades, n-type semiconductors such as TiO$_2$, WO$_3$, Fe$_2$O$_3$, and BiVO$_4$ have been extensively studied in the photoanode for PEC water oxidation.$^{11-18}$ However, there are relatively fewer stable and narrow band gap p-type candidates for the PEC water reduction to produce hydrogen fuel.

Cuprous oxide (Cu$_2$O), an intrinsic p-type semiconductor material, has gained significant interest in PEC water reduction because of its elemental abundance and scalable synthesis techniques.$^{19-36}$ Moreover, Cu$_2$O has a direct band gap energy of 2.0 eV, which enables a theoretical photocurrent density ($j_{ph}$) of 14.7 mA/cm$^2$ and a solar-to-hydrogen (STH) conversion efficiency of 18% under a standard 100 mW/cm$^2$ AM1.5G illumination.$^{19}$ However, the poor stability of Cu$_2$O in aqueous solutions hinders its PEC water splitting application.$^{20}$ Therefore, the protective layer and the hydrogen evolution reaction (HER) cocatalyst are required to coat on the photocathode.$^{37,38}$ Recently, Paracchino and co-workers reported a highly active and stable Cu$_2$O-based photocathode that was covered with a bilayer of 20 nm Al-doped ZnO and 10 nm TiO$_2$ and decorated with Pt nanoparticles as HER cocatalysts.$^{19,20}$ The p-Cu$_2$O/n-ZnO junction facilitated charge separation, and the TiO$_2$ layer played as a protection layer to improve stability. Furthermore, using RuO$_2$ as the HER cocatalyst, Luo and co-workers reported the enhanced PEC performance of the Cu$_2$O/AZO/TiO$_2$/RuO$_2$ photocathode.$^{26}$ In most reported studies, a thin TiO$_2$ layer was employed to protect Cu$_2$O against corrosion. However, one issue of using TiO$_2$ as the protective layer is that the photogenerated electrons accumulate in the TiO$_2$ layer and form Ti$^{3+}$ electron traps, thus resulting in a decreased photocurrent and low stability of the Cu$_2$O/ZnO/TiO$_2$ photocathode.$^{20}$ Moreover, because of the low HER activity of TiO$_2$, the noble metal cocatalysts such as Pt and RuO$_2$ are required to coat on TiO$_2$ to improve water reduction activity. In this work, we address...
these issues by a strategy to simultaneously protect Cu$_2$O and enhance its PEC water reduction performance, wherein the decorated NiO$_x$ layer enables an increased stability and an enhanced water reduction reaction.

NiO is optically transparent to the visible sunlight because of its wide band gap of $\sim$3.5 eV, which makes it a highly desirable protective layer for coating Cu$_2$O as it minimizes sunlight loss. Unlike the precious metal cocatalysts of Pt and RuO$_2$, the noble metal-free NiO cocatalyst has been identified as the choice of electrocatalytic material for HER in natural and alkaline electrolytes because of an optimal design stemming from their complementary bifunctional electrocatalytic activity. It has been reported that the NiO or NiO$_x$ coating on semiconductor photocathodes can improve the photocurrent and stability for water reduction. To the best of our knowledge, there is no demonstration of the integrated NiO$_x$ material on a Cu$_2$O/ZnO p-n junction photocathode for enhanced PEC water splitting.

Herein, with a coating of the NiO$_x$ layer as the protection layer and the HER cocatalyst, the noble metal-free Cu$_2$O/ZnO/NiO$_x$ photocathode promotes charge separation and transport for water reduction reaction. Notably, the outermost NiO$_x$ film performs dual function of protecting the Cu$_2$O photocathode against corrosion and improving the HER reduction activity. In the PEC water-splitting cell, we demonstrate a significantly enhanced photocurrent and remarkably increased stability of the Cu$_2$O/ZnO/NiO$_x$ photocathode. These results provide new insights into the development of noble metal-free photocathodes toward efficient solar hydrogen generation.

2. EXPERIMENTAL SECTION

2.1. Preparation of Cu$_2$O and ZnO. Prior to the deposition of Cu$_2$O, 10 nm gold (Au) was first deposited on the indium tin oxide (ITO) substrate by the vacuum evaporation technique, as it has been shown that Au forms a good Ohmic contact with p-type Cu$_2$O. Then, the ~250 nm Cu$_2$O film was deposited at 400 °C on the Au (10 nm)/ITO substrate in an O$_2$/Ar (7.5/42.5 sccm) atmosphere by reactive DC magnetron sputtering (Semicore Triaxis). Cu (99.99%) was used as the target, and the presputtering time was 10 min to avoid any contamination. The power was fixed at 100 W. During sputtering deposition, the base pressure was kept below $5 \times 10^{-7}$ Torr, and the sample stage was rotated at a constant speed of 12 rpm. Then, a ~50 nm Al-doped ZnO layer was deposited at 200 °C on Cu$_2$O in an Ar (50 sccm) atmosphere by radio frequency magnetron sputtering. The Al-doped ZnO (2 wt %) target was used with a power of 50 W. After Cu$_2$O/ZnO deposition, we prepared the TiO$_2$ and NiO$_x$ layers as the outer protective layer for a comparison.

2.2. Preparation of the Cu$_2$O/ZnO/TiO$_2$ Photocathode. The TiO$_2$ layer was deposited at 200 °C on Cu$_2$O/ZnO in an Ar (50 sccm) atmosphere by radio frequency magnetron sputtering from the TiO$_2$ (99.99%) target with a power of 50 W. The film thickness was determined using an ellipsometry (J. A. Woollam alpha-SE) instrument and modeled with Complete EASE software.

2.3. Preparation of the Cu$_2$O/ZnO/NiO$_x$ Photocathode. The Cu$_2$O/ZnO/NiO$_x$ photocathode was prepared by vacuum evaporation deposition of the 20 nm (or 200 nm) Ni film on the prepared Cu$_2$O/ZnO surface, followed by annealing at 400 °C for 30 min in air to form a NiO$_x$ film. For the study of the electrocatalytic properties of NiO$_x$, we also prepared the NiO$_x$ layers on ITO substrates under the same conditions.

2.4. Characterizations. PEC experiments were carried out in a typical three-electrode configuration in 0.1 M NaH$_2$PO$_4$ solution (NaPi, pH = 5) using a potentiostat (Princeton Applied Research, VersaSTAT 3). The electrolyte solution was purged with high purity (99.999%) Ar gas for over 30 min before PEC measurements. Standard simulated sunlight (AM1.5G 100 mW/cm$^2$) is generated from an AAA solar simulator (LOT-Quantum Design GmbH), which has been calibrated using a standard single-crystal Si photovoltaic cell. The working electrode areas of the Cu$_2$O, Cu$_2$O/ZnO, Cu$_2$O/ZnO/TiO$_2$, Cu$_2$O/ZnO/NiO$_x$-20 nm, and Cu$_2$O/ZnO/NiO$_x$-200 nm photocathodes are 1.0, 1.0, 1.0, 0.2, and 0.2 cm$^2$, respectively. A Pt plate (1 x 1 cm$^2$) and an Ag/AgCl (saturated KCl) electrode were used as the counter electrode and the reference electrode, respectively. Current density–potential ($j$–$V$) measurements were carried out at a scan rate of 30 mV/s with chopped illumination. The measured potential with respect to Ag/AgCl ($V_{Ag/AgCl}$) was converted to the potential versus reversible hydrogen electrode ($V_{RHE}$) using the following equation: $V_{RHE} = V_{Ag/AgCl} + 0.059 + x \times \text{pH}$, where $V_{Ag/AgCl}$ is the potential of the Ag/AgCl reference electrode with respect to the standard hydrogen potential. The incident photon-to-current efficiency (IPCE) was measured at 0 $V_{RHE}$ under chopped illuminations of different wavelengths of light-emitting diodes (LEDs, 1.0 mW/cm$^2$, spectral linewidth of 10 nm). The evolved H$_2$ gas was measured using a micro gas chromatograph (Agilent Technologies 490 Micro GC) at 0 $V_{RHE}$ under steady-state AM1.5G 100 mW/cm$^2$ illumination in 0.1 M NaPi solution, which was purged with high-purity Ar (99.999%) gas for over 30 min before the measurement. The Faradaic efficiency of H$_2$ gas evolution was determined by a comparison of the detected volume of H$_2$ gas and the calculated volumes of H$_2$ gas with a theoretical 100% Faradaic efficiency. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDXS) images were collected using an LEO 1550 Gemini instrument with an X-Max silicon drift detector (Oxford instruments). X-ray diffraction (XRD) was measured using a Philips MRD. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos Ultra photoelectron spectrometer equipped.

3. RESULTS AND DISCUSSION

To compare the PEC performance of the Cu$_2$O/ZnO photocathode with different protective layers, we prepared both the Cu$_2$O/ZnO/TiO$_2$ and Cu$_2$O/ZnO/NiO$_x$ photocathodes on the identical Cu$_2$O/ZnO samples. The morphology of the Cu$_2$O film was characterized by SEM images...
with a thickness of 50 nm was deposited on a Cu2O surface to form a p–n heterojunction (Figures S1B, S2B). As the Cu2O and ZnO layers suffer from corrosion in the electrolyte, a protective layer is required to coat Cu2O/ZnO. According to the reported studies,22,23 a TiO2 layer was deposited to coat the Cu2O/ZnO electrode because of its chemical stability and visible-sunlight transparent advantage (band gap ∼3.2 eV). The SEM image shows that the thickness of the TiO2 layer is about 250 nm, and the surface morphology displays that the grain size of TiO2 is around ∼150 nm (Figures 1A, S1C, S2C). Figure 1B shows the XRD patterns of Cu2O, Cu2O/ZnO, and Cu2O/ZnO/TiO2 samples. The diffraction peaks confirm the deposition of Cu2O, ZnO, and TiO2 layers, according to the JCPDS cards of no. 78-2076, 36-1451, and 21-1272, respectively.

Figure 1C compares the PEC performance of the Cu2O, Cu2O/ZnO, and Cu2O/ZnO/TiO2 photocathodes in an Ar-purged 0.1 M NaH2PO4 (NaPi) electrolyte (pH = 5.0). The photocurrent behavior of the Cu2O/ZnO/TiO2 photocathode shows a significantly reduced dark current (Figure 1C). The XRD results of Cu2O/ZnO/TiO2 show identical diffraction peaks before and after PEC measurements, while the surface morphology remains unchanged, indicating the protective effect of the TiO2 layer (Figures 1B, and S1–2). However, the j–V curve of the Cu2O/ZnO/TiO2 photocathode still shows a slight decrease in photocurrent in the second j–V scan (Figure S3C). Considering that the structure and morphology of Cu2O/ZnO/TiO2 remain unchanged with the protection layer of 250 nm TiO2, the photocurrent decay is attributed to the formation of the Ti3+ electron traps in the TiO2 layer during the PEC reaction. Paracchino et al. reported that the photogenerated electrons accumulate in the TiO2 layer to form Ti3+ electron traps, thus resulting in a decreased photocurrent and low stability of the Cu2O/ZnO/TiO2 photocathode for PEC water splitting.20 Moreover, TiO2 has a low electrocatalytic activity for water reduction, and noble metal cocatalysts (such as Pt and RuO2) are generally required to coat TiO2 as described in previous studies.19,26

To overcome these drawbacks of the Cu2O/ZnO/TiO2 structure and noble metal cocatalysts, we employ the NiOx layer as both a protective and HER catalytic layer to fabricate a noble metal-free photocathode of Cu2O/ZnO/NiOx. The HER activity of NiOx has been demonstrated on other semiconductor photocathodes.40–43 In this work, we develop a facile approach to prepare the NiOx layers. First, the 200 nm Ni layer was deposited on ITO substrates, followed by annealing at 400 °C in air for 5, 15, 30, and 60 min. As seen in Figure 2A, XRD patterns of the annealed samples exhibit the peaks of NiO accompanied with small peaks of Ni, indicating that the deposited Ni was oxidized to a mixture of NiO and Ni (denoted as NiOx). This result is further confirmed by the XPS measurement, as discussed below. Figure 2B,C shows the j–V curves and the corresponding Tafel plots of ITO, ITO/Ni, and ITO/NiOx with different annealing times. Compared to ITO or the Ni electrode, the NiOx samples exhibit a remarkably enhanced HER activity for water reduction. In particular, the NiOx annealed for 30 min shows the lowest overpotential (requiring a very low overpotential of 115 mV to drive 10 mA cm−2) and the smallest Tafel slope (35.9 mV/dec), which are very close to the HER activity of the Pt electrode measured under the same conditions (Tafel slope of the Pt electrode: 32.5 mV/dec). This result clearly demonstrates that the prepared NiOx exhibits as high HER activity as the well-developed noble metal HER cocatalysts. Therefore, we employ this NiOx preparation condition to fabricate the Cu2O/ZnO/NiOx photocathode.
The SEM image of Cu2O/ZnO/NiO exhibits a dense layer of NiO nanoparticles (Figures 3A and S4). The top view SEM image and the corresponding EDXS data show the Ni, Zn, O elements in the Cu2O/ZnO/NiO region (Figure S5). The EDXS results show that the elemental components of the deposited nanoparticles are Ni and O. The XRD results of Cu2O/ZnO/NiO exhibit the diffraction peaks of Cu2O, ZnO, and NiO (Figure S3B), further confirming the formation of NiO on Cu2O/ZnO.

The surface composition and chemical states of the NiO layer were characterized by the XPS measurements. As shown in Figure S6, the Ni 2p spectrum displays the typical characteristics of the presence of Ni0 and Ni2+ species. The fitting peaks at 852.1, 856.8, and 858.6 eV are ascribed to the Ni 2p3/2 peaks of Ni2+ species (NiO), with three satellite peaks at high binding energy (861.3, 864.0, and 866.4 eV, respectively). The Ni 2p1/2 peaks of Ni2+ species (NiO), with three satellite peaks at high binding energy (861.3, 864.0, and 866.4 eV, respectively).

The PEC water splitting measurements of Cu2O/ZnO/NiO were performed in 0.1 M NaPi electrolyte (pH = 5.0) under chopped AM1.5G 100 mW/cm² illumination. The PEC water splitting measurements of Cu2O/ZnO/NiO exhibit a significantly enhanced photocurrent, indicating the efficient HER activity of NiO, as demonstrated by the electrocatalytic measurements in Figure 2B.C. Moreover, the XRD pattern and SEM image of the Cu2O/ZnO/NiO photocathode do not show any observable changes before and after PEC measurements (Figures 3B and S4). These results further confirm that the 200 nm NiO layer protects Cu2O/ZnO against corrosion. As a comparison, with a thinner NiO layer (20 nm) as a protective layer, the j-V curve of the Cu2O/ZnO/NiO-20 nm photocathode shows a larger dark current (Figure 3C), indicating an inefficient protection against corrosion.

The applied-bias photon-to-current efficiency (ABPE) of the Cu2O-based photocathodes was derived using the equation: ABPE (%) = \( j_{ph} \times (E - E^{0}_{rev}) / P_n \times 100 \), where \( E^{0}_{rev} \) is 0 V_RHE, \( E \) is the applied potential in V_RHE, and \( P_n \) is the power of the incident light (100 mW/cm²). As shown in Figure 3D, the maximum ABPE of the Cu2O/ZnO/NiO-200 nm photocathode is 0.07% at 0.19 V_RHE, which is much higher than that of the Cu2O/ZnO photocathode (0.01% at around 0.1 V_RHE). Although the thinner NiO (20 nm) gives rise to a higher maximum ABPE of 0.11% at 0.26 V_RHE, the dark current is obviously increased because of the inefficient protection against corrosion. It is worthwhile mentioning that the applied potentials for the maximum ABPE are positive-shifted for the photocathodes with coating NiO layers, indicating the reduced overpotentials for the H2-evolution reaction on NiO. The incident photon-to-current efficiency (IPCE) of the Cu2O/ZnO/NiO-200 nm photocathode was measured at 0 V_RHE under chopped illuminations of different wavelengths of LEDs (1.0 mW/cm², spectral linewidth of 10 nm) (Figure S7). The highest IPCE of 63.6% is obtained for the Cu2O/ZnO/NiO-200 nm photocathode at 450 nm.

The stability of the photocathodes and the evolved H2 gas was measured under steady-state AM1.5G 100 mW/cm² illumination. As shown in Figure 3E, the chronoamperometry
Cu2O/ZnO/NiO

do not hallucinate.

The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 1 to \(10^5\) Hz, at 0 V_RHE in 0.1 M NaPi (pH = 5.0), under AM1.5G 100 mW/cm² illumination. The EIS data were fitted using the equivalent circuits (left inset for Cu2O and Cu2O/ZnO photocathodes and right inset for Cu2O/ZnO/TiO2-250 nm and Cu2O/ZnO/NiO2-200 nm photocathodes). Figure 4A shows the Nyquist plots of the Cu2O/ZnO/NiO2-200 nm photocathode. The Nyquist plots show two semicircles, which can be fitted by the equivalent circuits shown in the right inset of Figure 4A. The fitting results show that Cu2O/ZnO/TiO2 and Cu2O/ZnO/NiO2 have a similar value of charge-transfer resistance from the bulk to the photocathode surface, \(R_{ct,1} = 100\ \Omega\ cm^2\) for Cu2O/ZnO/TiO2 and \(R_{ct,1} = 90\ \Omega\ cm^2\) for Cu2O/ZnO/NiO2. However, Cu2O/ZnO/TiO2 exhibits a rather large resistance of 2200\ \Omega\ cm² for the charge-transfer across the electrode/electrolyte interface (\(R_{ct,2}\)). In contrast, the Cu2O/ZnO/NiO2 displays a significantly decreased resistance \(R_{ct,2}\) of 400\ \Omega\ cm² (Table S1). Figure 4B illustrates a schematic energy band diagram of the Cu2O/ZnO/NiO2 photocathode, \(E_{CB}\) and \(E_{VB}\) where the built-in electric field in the Cu2O/ZnO p–n junction separates the photogenerated electron–hole pairs and sweeps the electrons to the NiO2 catalyst for water reduction. Given the fact of similar thickness of TiO2 and NiO2 and the identical Cu2O/ZnO p–n junction underneath, the charge transfer resistance in the bulk of the Cu2O/ZnO/TiO2 and Cu2O/ZnO/NiO2 photocathodes is mainly affected by the built-in electric field and bulk recombination (Figure 4B), which give rise to a similar value of \(R_{ct,1}\). The remarkably reduced value of \(R_{ct,2}\) for Cu2O/ZnO/NiO2 is mainly resulting from the presence of the high HER activity NiO2 catalyst as demonstrated in Figure 2B. This result further confirms that NiO2 is not only a stable protective layer against corrosion but also a highly active H2 evolution cocatalyst, distinctly outperforming the TiO2 layer.

In summary, we have demonstrated a strategy of using NiO2 as a protective layer and the HER cocatalyst to improve the stability and the efficiency of the Cu2O photocathode for H2 evolution. We report a facile approach to fabricate the NiO2 layer by Ni oxidation. The optimized NiO2 layer exhibits a very low overpotential of 115 mV to drive 10 mA cm⁻² and a small Tafel slope of 35.9 mV/dec, which are very close to the HER activity of the Pt electrode. With a decorated 200 nm NiO2 layer on the Cu2O/ZnO p–n junction, the photocathode shows a synergetic enhancement of both the photocurrent and the Faradaic efficiency for H2 evolution. The EIS results evidence that the NiO2 layer significantly reduces the charge transfer resistance for water reduction. By comparison with the mostly used TiO2 layer, this work unambiguously demonstrates the dual functions of NiO2 as a protective layer and a

To understand the enhancement of the PEC performance of the Cu2O/ZnO/NiO2 photocathodes, EIS measurements were carried out in the frequency range of 1 to \(10^5\) Hz, at 0 V_RHE in 0.1 M NaPi (pH = 5.0), under AM1.5G 100 mW/cm² illumination. Figure 4A shows the Nyquist plots of the Cu2O, Cu2O/ZnO, Cu2O/ZnO/TiO2-250 nm, and Cu2O/ZnO/NiO2-200 nm photocathodes. The Nyquist plots show a quite stable \(j_{ph}\) of around –0.77 mA/cm² at 0 V_RHE over 90 min illumination. As a comparison, the \(j_{ph}\) of the Cu2O/ZnO/NiO2-20 nm photocathode is decreased to 0.84 mA/cm² after 90 min of illumination (76% of its initial photocurrent), and the photocurrent of the Cu2O/ZnO photocathode is significantly decreased in 30 min (Figure 3E). Meanwhile, the volumes of the evolved H2 gas were measured by gas chromatography to evaluate the Faradaic efficiencies (\(\eta_{Fe}\)) of H2. As shown in Figure 3F, the Cu2O/ZnO photocathode exhibits a low \(\eta_{Fe}\) of 35 ± 9% for H2 evolution because of the serious corrosion. With coating NiO, the Cu2O/ZnO/NiO2-20 nm photocathode exhibits an \(\eta_{Fe}\) of 93 ± 3% for H2 evolution. Furthermore, a higher H2 evolution efficiency of 95 ± 4% is obtained with further increasing the thickness of the NiO2 layer to 200 nm. These results show that the Cu2O/ZnO/NiO2 photocathode demonstrates a synergetic enhancement of both the photocurrent and the Faradaic efficiency for H2 evolution, unambiguously indicating the dual functions of NiO2 as a protective layer and a highly active HER catalyst to improve the PEC performance of Cu2O. Compared to the reported Cu2O/ZnO/TiO2/RuO2 and Cu2O/ZnO/TiO2/Pt and other heterojunction photocathodes,\(^{35,36,37}\) this work demonstrates a facile approach to fabricate the noble metal-free photocathode using NiO2 to replace both the TiO2 and RuO2(Pt) layers (Table S1).

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![Figure 4. (A) Nyquist plots of the Cu2O, Cu2O/ZnO, Cu2O/ZnO/TiO2-250 nm, and Cu2O/ZnO/NiO2-200 nm photocathodes. The Nyquist plots show two semicircles, which can be fitted by the equivalent circuits shown in the right inset of Figure 4A. The fitting results show that Cu2O/ZnO/TiO2 and Cu2O/ZnO/NiO2 have a similar value of charge-transfer resistance from the bulk to the photocathode surface, \(R_{ct,1} = 100\ \Omega\ cm^2\) for Cu2O/ZnO/TiO2 and \(R_{ct,1} = 90\ \Omega\ cm^2\) for Cu2O/ZnO/NiO2. However, Cu2O/ZnO/TiO2 exhibits a rather large resistance of 2200\ \Omega\ cm² for the charge-transfer across the electrode/electrolyte interface (\(R_{ct,2}\)). In contrast, the Cu2O/ZnO/NiO2 displays a significantly decreased resistance \(R_{ct,2}\) of 400\ \Omega\ cm² (Table S1). Figure 4B illustrates a schematic energy band diagram of the Cu2O/ZnO/NiO2 photocathode, \(E_{CB}\) and \(E_{VB}\) where the built-in electric field in the Cu2O/ZnO p–n junction separates the photogenerated electron–hole pairs and sweeps the electrons to the NiO2 catalyst for water reduction. Given the fact of similar thickness of TiO2 and NiO2 and the identical Cu2O/ZnO p–n junction underneath, the charge transfer resistance in the bulk of the Cu2O/ZnO/TiO2 and Cu2O/ZnO/NiO2 photocathodes is mainly affected by the built-in electric field and bulk recombination (Figure 4B), which give rise to a similar value of \(R_{ct,1}\). The remarkably reduced value of \(R_{ct,2}\) for Cu2O/ZnO/NiO2 is mainly resulting from the presence of the high HER activity NiO2 as demonstrated in Figure 2B. This result further confirms that NiO2 is not only a stable protective layer against corrosion but also a highly active H2 evolution cocatalyst, distinctly outperforming the TiO2 layer.

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highly active HER catalyst for improving both the stability and the PEC water splitting performance of Cu2O. These findings shed light on the design of noble metal-free photoelectrodes for solar fuel development.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c01198.

SEM of photocathodes before and after PEC measurements, PEC measurement results, and EDS and fitting results of the EIS data (PDF)

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### Notes

The authors declare no competing financial interest.

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