Cu₂O/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 (Cu₂O) 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 TiO₂ and noble metal cocatalysts for coating the Cu₂O photocathode, this work demonstrates a strategy to fabricate a noble metal-free photocathode. We construct a Cu₂O/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/cm², which are very close to the HER activity of the noble metal platinum. With decorated NiO_x, the Cu₂O/ZnO/NiO_x photocathode exhibits significantly improved stability and photocurrent density with a Faradaic efficiency of H₂ gas evolution of 95 ± 4%, distinctly outperforming the Cu₂O, Cu₂O/ZnO, and Cu₂O/ZnO/TiO₂ 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 H₂ 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 TiO₂, WO₃, Fe₂O₃, and BiVO₄ 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 (Cu₂O), 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, Cu₂O has a direct band gap energy of 2.0 eV, which enables a theoretical photocurrent density (*j_{ph}*) of 14.7 mA/cm² and a solar-to-hydrogen (STH) conversion efficiency of 18% under a standard 100 mW/cm² AM1.5G illumination.¹⁹ However, the poor stability of Cu₂O 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 Cu₂O-based photocathode that was covered with a bilayer of 20 nm Al-doped ZnO and 10 nm TiO₂ and decorated with Pt nanoparticles as HER cocatalysts.^{19,20} The p-Cu₂O/n-ZnO junction facilitated charge separation, and the TiO₂ layer played as a protection layer to improve stability. Furthermore, using RuO₂ as the HER cocatalyst, Luo and co-workers reported the enhanced PEC performance of the Cu₂O/AZO/TiO₂/RuO₂ photocathode.²⁶ In most reported studies, a thin TiO₂ layer was employed to protect Cu₂O against corrosion. However, one issue of using TiO₂ as the protective layer is that the photogenerated electrons accumulate in the TiO₂ layer and form Ti³⁺ electron traps, thus resulting in a decreased photocurrent and low stability of the Cu₂O/ZnO/TiO₂ photocathode.²⁰ Moreover, because of the low HER activity of TiO₂, the noble metal cocatalysts such as Pt and RuO₂ are required to coat on TiO₂ to improve water reduction activity. In this work, we address

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Figure 1. (A) Cross-sectional SEM image of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{TiO}_2$ photocathode. (B) XRD patterns of Cu_2O , $\text{Cu}_2\text{O}/\text{ZnO}$, and $\text{Cu}_2\text{O}/\text{ZnO}/\text{TiO}_2$ photocathodes before and after (denoted with star marks) PEC water splitting measurements. (C) j - V curves of Cu_2O , $\text{Cu}_2\text{O}/\text{ZnO}$, and $\text{Cu}_2\text{O}/\text{ZnO}/\text{TiO}_2$ photocathodes in 0.1 M NaPi electrolyte solution (pH = 5) under chopped AM1.5G 100 mW/cm^2 illumination.

these issues by a strategy to simultaneously protect Cu_2O 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 ~ 3.5 eV,³⁹ which makes it a highly desirable protective layer for coating Cu_2O 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.^{40–43} To the best of our knowledge, there is no demonstration of the integrated NiO_x material on a $\text{Cu}_2\text{O}/\text{ZnO}$ 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 $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ photocathode promotes charge separation and transport for water reduction reaction. Notably, the outermost NiO_x film performs dual function of protecting the Cu_2O 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 $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ 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_2O and ZnO . Prior to the deposition of Cu_2O , 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_2O .²³ Then, the ~ 250 nm Cu_2O 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).⁴⁴ Cu (99.99%) was used as a 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 5×10^{-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_2O 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 $\text{Cu}_2\text{O}/\text{ZnO}$ deposition, we prepared the TiO_2 and NiO_x layers as the outer protective layer for a comparison.

2.2. Preparation of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{TiO}_2$ Photocathode. The TiO_2 layer was deposited at 200 °C on $\text{Cu}_2\text{O}/\text{ZnO}$ 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. Woolam alpha-SE) instrument and modeled with Complete EASE software.

2.3. Preparation of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ Photocathode. The $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ photocathode was prepared by vacuum evaporation deposition of the 20 nm (or 200 nm) Ni film on the prepared $\text{Cu}_2\text{O}/\text{ZnO}$ 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_2PO_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_2O , $\text{Cu}_2\text{O}/\text{ZnO}$, $\text{Cu}_2\text{O}/\text{ZnO}/\text{TiO}_2$, $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -20 nm, and $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -200 nm photocathodes are 1.0, 1.0, 1.0, 0.2, and 0.2 cm^2 , respectively. A Pt plate (1 $\times$ 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 ($V_{\text{Ag/AgCl}}$) was converted to the potential versus reversible hydrogen electrode (V_{RHE}) using the following equation: $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + V_0 + 0.059 \times \text{pH}$, where V_0 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 $\text{Cu}_2\text{O}/\text{ZnO}$ photocathode with different protective layers, we prepared both the $\text{Cu}_2\text{O}/\text{ZnO}/\text{TiO}_2$ and $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ photocathodes on the identical $\text{Cu}_2\text{O}/\text{ZnO}$ samples. The morphology of the Cu_2O film was characterized by SEM images

Figure 2. XRD patterns (A), *j*-*V* curves (B), and Tafel plots (C) of ITO, ITO/Ni, and ITO/NiO_x electrodes after annealing at 400 °C for 5, 15, 30, and 60 min. The electrochemical experiments are measured in 0.1 M NaPi electrolyte solution (pH = 5) in the dark at a scan rate of 10 mV/s. The Pt plate electrode was tested under the same condition as a controlled reference.

(Figure S1A). As shown in SEM images, the Cu₂O film was composed of nanoparticles and approximately 250 nm in thickness (Figure S2A). Following, the n-type Al-doped ZnO 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,^{19,23} 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 current density–potential (*j*-*V*) curves were measured under the chopped 100 mW/cm² AM1.5G illumination, so the dark and light current could be monitored simultaneously. Notably, the bare Cu₂O photocathode exhibits a significant dark current below 0.25 V_{RHE}, which is assigned to the reductive decomposition of the Cu₂O material according to reaction 1¹⁹

To check the stability of the Cu₂O photocathode, the second scan was carried out. As shown in Figure S3A, the photocurrent behavior of the Cu₂O photocathode substantially disappeared, leaving only a significant Cu₂O reduction peak at around 0.2 V_{RHE}. Reductive decomposition of the Cu₂O electrode is visually observed by the formation of a black film (Cu) where the electrode is illuminated. As shown in Figure 1B, the XRD pattern displays that the diffraction peaks of Cu₂O disappeared after PEC water splitting measurements. SEM images confirm that the nanostructure of the Cu₂O layer has been destroyed after PEC measurements (Figures S1D, S2D).

The Cu₂O/ZnO photocathode also exhibits a large dark current and an unrepeatable *j*-*V* behavior under chopped illumination (Figures 1C, S3B). The XRD result shows reduced diffraction peaks of Cu₂O after PEC measurements (Figure 1B). The SEM images display a deteriorated surface of Cu₂O/ZnO after PEC measurements, indicating that the ZnO layer was etched in the weak acid electrolyte during the PEC reaction (Figures S1E, S2E).

With the deposition of 250 nm-thick TiO₂, 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 NiO_x layer as both a protective and HER catalytic layer to fabricate a noble metal-free photocathode of Cu₂O/ZnO/NiO_x. The HER activity of NiO_x has been demonstrated on other semiconductor photocathodes.^{40–43} In this work, we develop a facile approach to prepare the NiO_x 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 NiO_x). 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/NiO_x with different annealing times. Compared to ITO or the Ni electrode, the NiO_x samples exhibit a remarkably enhanced HER activity for water reduction. In particular, the NiO_x 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 NiO_x exhibits as high HER activity as the well-developed noble metal HER cocatalysts. Therefore, we employ this NiO_x preparation condition to fabricate the Cu₂O/ZnO/NiO_x photocathode.

Figure 3. (A) Cross-sectional SEM image of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -200 nm photocathode. (B) XRD patterns of $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -200 nm before and after (denoted with star) PEC water splitting measurements. The j - V curves (C) and ABPE plots (D) of the $\text{Cu}_2\text{O}/\text{ZnO}$, $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -20 nm, and $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -200 nm photocathodes in 0.1 M NaPi electrolyte solution (pH = 5) under chopped AM1.5G 100 mW/cm^2 illumination. The j - t curves (E) and the evolved H_2 gas (F) of the $\text{Cu}_2\text{O}/\text{ZnO}$, $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -20 nm, and $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -200 nm photocathodes measured at 0 V_{RHE} under steady-state AM1.5G 100 mW/cm^2 illumination in 0.1 M NaPi solution. The dotted lines in (F) represent the calculated volumes of H_2 gas with a theoretical 100% Faradaic efficiency.

The SEM image of $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ exhibits a dense layer of NiO_x nanoparticles (Figures 3A and S4). The top view SEM image and the corresponding EDXS measured on the boundary between the $\text{Cu}_2\text{O}/\text{ZnO}$ region and the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ region display the Cu, Zn, and O elements in the $\text{Cu}_2\text{O}/\text{ZnO}$ region and Ni and O elements in the NiO_x region (Figure S5). The EDXS results show that the elemental components of the deposited nanoparticles are Ni and O. The XRD results of $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ exhibit the diffraction peaks of Cu_2O , ZnO , and NiO_x (Figure 3B), further confirming the formation of NiO_x on $\text{Cu}_2\text{O}/\text{ZnO}$.

The surface composition and chemical states of the NiO_x layer were characterized by the XPS measurements. As shown in Figure S6, the Ni 2p spectrum displays the typical characteristics of the presence of Ni^0 and Ni^{2+} species. The fitting peaks at 852.1, 856.8, and 858.6 eV are ascribed to the Ni 2p_{3/2} and two satellite peaks of nickel metal (Ni^0 species), respectively.⁴⁵ The fitting peaks at 853.7 and 855.5 eV are attributed to two Ni 2p_{3/2} peaks of Ni^{2+} species (NiO), with three satellite peaks at high binding energy (861.3, 864.0, and 866.4 eV, respectively).^{46,47} From the area of Ni 2p_{3/2} peaks of Ni^0 and Ni^{2+} , the composition of the NiO_x catalyst prepared by annealing Ni at 400 °C (in air, for 30 min) is estimated to be 16.8% of Ni and 83.2% of NiO . Additionally, the O 1s spectrum shown in Figure S6 exhibits two peaks at 529.3, 531.1, and 532.4 eV, which have been attributed to the lattice oxygen and the surface-adsorbed hydroxyl groups and water molecules, respectively.

The PEC water splitting measurements of $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ photocathodes were carried out in an Ar-purged 0.1 M NaPi electrolyte (pH = 5.0) under chopped AM1.5G 100 mW/cm^2 illumination. Figure 3C compares the j - V curves of the $\text{Cu}_2\text{O}/\text{ZnO}$ and $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ photocathodes. With the deposition of 200 nm NiO_x , the dark current is significantly reduced and the photocurrent j_{ph} is enhanced to $-0.84 \text{ mA}/\text{cm}^2$ at 0 V_{RHE} , together with a positive-shifted onset potential E_{onset} to $\sim 0.6 V_{\text{RHE}}$. The decreased dark current indicates that the NiO_x protects $\text{Cu}_2\text{O}/\text{ZnO}$ against corrosion. Compared to the

$\text{Cu}_2\text{O}/\text{ZnO}/\text{TiO}_2$ photocathode with 250 nm TiO_2 as the protective layer (j_{ph} : $-0.10 \text{ mA}/\text{cm}^2$ at 0 V_{RHE}), the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ photocathode exhibits a significantly enhanced photocurrent, indicating the efficient HER activity of NiO_x , as demonstrated by the electrocatalytic measurements in Figure 2B,C. Moreover, the XRD pattern and SEM image of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ 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_x layer protects $\text{Cu}_2\text{O}/\text{ZnO}$ against corrosion. As a comparison, with a thinner NiO_x layer (20 nm) as a protective layer, the j - V curve of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -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 Cu_2O -based photocathodes was derived using the equation: $\text{ABPE} (\%) = j_{\text{ph}} \times (E - E_{\text{rev}}^0) / P_{\text{in}} \times 100$, where E_{rev}^0 is 0 V_{RHE} , E is the applied potential in V_{RHE} , and P_{in} is the power of the incident light (100 mW/cm^2). As shown in Figure 3D, the maximum ABPE of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -200 nm photocathode is 0.07% at 0.19 V_{RHE} , which is much higher than that of the $\text{Cu}_2\text{O}/\text{ZnO}$ photocathode (0.01% at around 0.1 V_{RHE}). Although the thinner NiO_x (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_x layers, indicating the reduced overpotentials for the H_2 -evolution reaction on NiO_x . The incident photon-to-current efficiency (IPCE) of the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -200 nm photocathode was measured at 0 V_{RHE} under chopped illuminations of different wavelengths of LEDs (1.0 mW/cm^2 , spectral linewidth of 10 nm) (Figure S7). The highest IPCE of 63.6% is obtained for the $\text{Cu}_2\text{O}/\text{ZnO}/\text{NiO}_x$ -200 nm photocathode at 450 nm.

The stability of the photocathodes and the evolved H_2 gas was measured under steady-state AM1.5G 100 mW/cm^2 illumination. As shown in Figure 3E, the chronoamperometry

Figure 4. (A) Nyquist plots of the Cu_2O , $\text{Cu}_2\text{O/ZnO}$, $\text{Cu}_2\text{O/ZnO/TiO}_2$ -250 nm, and $\text{Cu}_2\text{O/ZnO/NiO}_x$ -200 nm photocathodes. 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/cm^2 illumination. The EIS data were fitted using the equivalent circuits (left inset for Cu_2O and $\text{Cu}_2\text{O/ZnO}$ photocathodes and right inset for $\text{Cu}_2\text{O/ZnO/TiO}_2$ -250 nm and $\text{Cu}_2\text{O/ZnO/NiO}_x$ -200 nm photocathodes). (B) Schematic energy band diagram of the $\text{Cu}_2\text{O/ZnO/NiO}_x$ photocathode.

($j-t$) curve of the $\text{Cu}_2\text{O/ZnO/NiO}_x$ -200 nm photocathode exhibits a quite stable j_{ph} of around -0.77 mA/cm^2 at 0 V_{RHE} over 90 min illumination. As a comparison, the j_{ph} of the $\text{Cu}_2\text{O/ZnO/NiO}_x$ -20 nm photocathode is decreased to 0.84 mA/cm^2 after 90 min of illumination (76% of its initial photocurrent), and the photocurrent of the $\text{Cu}_2\text{O/ZnO}$ photocathode is significantly decreased in 30 min (Figure 3E). Meanwhile, the volumes of the evolved H_2 gas were measured by gas chromatography to evaluate the Faradaic efficiencies (η_{F}) of H_2 . As shown in Figure 3F, the $\text{Cu}_2\text{O/ZnO}$ photocathode exhibits a low η_{F} of $35 \pm 9\%$ for H_2 evolution because of the serious corrosion. With coating NiO_x , the $\text{Cu}_2\text{O/ZnO/NiO}_x$ -20 nm photocathode exhibits an η_{F} of $93 \pm 3\%$ for H_2 evolution. Furthermore, a higher H_2 evolution efficiency of $95 \pm 4\%$ is obtained with further increasing the thickness of the NiO_x layer to 200 nm. These results show that the $\text{Cu}_2\text{O/ZnO/NiO}_x$ photocathode demonstrates a synergetic enhancement of both the photocurrent and the Faradaic efficiency for H_2 evolution, unambiguously indicating the dual functions of NiO_x as a protective layer and a highly active HER catalyst to improve the PEC performance of Cu_2O . Compared to the reported $\text{Cu}_2\text{O/ZnO/TiO}_2/\text{RuO}_2$ and $\text{Cu}_2\text{O/ZnO/TiO}_2/\text{Pt}$ and other heterojunction photocathodes,^{25,26,32} this work demonstrates a facile approach to fabricate the noble metal-free photocathode using NiO_x to replace both the TiO_2 and $\text{RuO}_2(\text{Pt})$ layers (Table S1).

To understand the enhancement of the PEC performance of the $\text{Cu}_2\text{O/ZnO/NiO}_x$ photocathode, 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/cm^2 illumination. Figure 4A shows the Nyquist plots of the Cu_2O , $\text{Cu}_2\text{O/ZnO}$, $\text{Cu}_2\text{O/ZnO/TiO}_2$ -250 nm, and $\text{Cu}_2\text{O/ZnO/NiO}_x$ -200 nm photocathodes. The EIS data were fitted using the equivalent circuits shown in the insets. As shown in Figure 4A, the $\text{Cu}_2\text{O/ZnO}$ photocathode exhibits a smaller diameter of the semicircle compared to Cu_2O . The fitting results reveal that the value of charge-transfer resistance (R_{ct}) is decreased from 700 $\Omega \text{ cm}^2$ for Cu_2O to 520 $\Omega \text{ cm}^2$ for $\text{Cu}_2\text{O/ZnO}$ (Table S2). This can be explained by the built-in electric field in the $\text{Cu}_2\text{O/ZnO}$ p-n junction that promotes charge separation, thus reducing the charge transfer resistance (Figure 4B). With a coating of 250 nm TiO_2 or 200 nm NiO_x , 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 $\text{Cu}_2\text{O/ZnO/TiO}_2$ and $\text{Cu}_2\text{O/ZnO/NiO}_x$ have a similar value of charge-transfer resistance from the bulk to the photocathode surface, $R_{\text{ct},1}$ ($R_{\text{ct},1} = 100 \Omega \text{ cm}^2$ for $\text{Cu}_2\text{O/ZnO/TiO}_2$ and $R_{\text{ct},1} = 90 \Omega \text{ cm}^2$ for $\text{Cu}_2\text{O/ZnO/NiO}_x$). However, $\text{Cu}_2\text{O/ZnO/TiO}_2$ exhibits a rather large resistance of 2200 $\Omega \text{ cm}^2$ for the charge-transfer across the electrode/electrolyte interface ($R_{\text{ct},2}$). In contrast, the $\text{Cu}_2\text{O/ZnO/NiO}_x$ displays a significantly decreased resistance $R_{\text{ct},2}$ of 400 $\Omega \text{ cm}^2$ (Table S1). Figure 4B illustrates a schematic energy band diagram of the $\text{Cu}_2\text{O/ZnO/NiO}_x$ photocathode,^{19,20,48} where the built-in electric field in the $\text{Cu}_2\text{O/ZnO}$ p-n junction separates the photogenerated electron-hole pairs and sweeps the electrons to the NiO_x catalyst for water reduction. Given the fact of similar thickness of TiO_2 and NiO_x and the identical $\text{Cu}_2\text{O/ZnO}$ p-n junction underneath, the charge transfer resistance in the bulk of the $\text{Cu}_2\text{O/ZnO/TiO}_2$ and $\text{Cu}_2\text{O/ZnO/NiO}_x$ photocathodes is mainly affected by the built-in electric field and bulk recombination (Figure 4B), which give rise to a similar value of $R_{\text{ct},1}$. The remarkably reduced value of $R_{\text{ct},2}$ for $\text{Cu}_2\text{O/ZnO/NiO}_x$ is mainly resulting from the presence of the high HER activity NiO_x , as demonstrated in Figure 2B. This result further confirms that NiO_x is not only a stable protective layer against corrosion but also a highly active H_2 evolution cocatalyst, distinctly outperforming the TiO_2 layer.

In summary, we have demonstrated a strategy of using NiO_x as a protective layer and the HER cocatalyst to improve the stability and the efficiency of the Cu_2O photocathode for H_2 evolution. We report a facile approach to fabricate the NiO_x layer by Ni oxidation. The optimized NiO_x 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 NiO_x layer on the $\text{Cu}_2\text{O/ZnO}$ p-n junction, the photocathode shows a synergetic enhancement of both the photocurrent and the Faradaic efficiency for H_2 evolution. The EIS results evidence that the NiO_x layer significantly reduces the charge transfer resistance for water reduction. By comparison with the mostly used TiO_2 layer, this work unambiguously demonstrates the dual functions of NiO_x as a protective layer and a

highly active HER catalyst for improving both the stability and the PEC water splitting performance of Cu_2O . 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

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