Room Temperature Electrodeposition of Ready-to-Use TiO$_x$ for Uniform p-n Heterojunction Over Nanoarchitecture

Yufeng Cao$^1$, Huajian Qiao$^1$, Yalong Zou$^1$, Na An$^1$, Yang Zhou$^1$, Deyu Liu$^{1,2,*}$ and Yongbo Kuang$^{1,2,*}$

$^1$Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China, $^2$Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, China

The photocathodes are essential in photoelectrochemical systems for harvesting solar energy as green fuels. However, the light-absorbing p-type semiconductor in them usually suffers from carrier recombination issues. An effective strategy to address it is fabricating the p-n heterojunction to create an interfacial electric field. However, plenty of deposition process of the n-type layer for this purpose requires either sophisticated instruments or subsequent treatments, which may damage the vulnerable p-type structure. Herein, we report a mild approach for a ready-to-use n-type layer with full functionality. Structural analyses proved the successful coating of a uniform titania layer (up to 40 nm) over Cu$_2$O without damaging its structure. Owing to the high Ti$^{3+}$ content, the layer possesses excellent charge transport ability and requires no additional annealing. The heterojunction effectively facilitates the carrier separation and positively shifts the photocurrent onset potential for 0.2 V. The Mott–Schottky plot and the impedance study reveal an enhanced carrier collection with reduced charge transfer resistances. Such a nano-heterojunction can be further loaded with the hydrogen evolution catalyst, which almost doubles the photocurrent with an extended lifetime than that of the pristine Cu$_2$O nanoarray. This approach puts forward a potentially scalable and efficient choice for fabricating photoelectrochemical devices.

Keywords: titanium oxide, electrochemical deposition, heterogeneous nanostructure, cuprous oxide photocathode, p-n junction

INTRODUCTION

Oxide photocathodes have attracted great attention for the photoelectrocatalytic production of hydrogen fuels by solar water splitting (Li et al., 2020). Particularly, Cu$_2$O has been demonstrated as one of the most promising choices among many light-absorbing materials. The intrinsic Cu vacancies as shallow acceptor levels lead to decent p-type characteristics (Olsen et al., 1982). However, challenges are limiting the performance of photocathodes. Specifically, many photoelectodes suffer from surface redox instability and self-reduction by the interfacial accumulation of photoelectrons (Tilley et al., 2014). More importantly, the unsatisfactory charge separation and internal charge transport strongly degrade the practical efficiency from the theoretical expectation (Wick and Tilley, 2015; Luo et al., 2016). The short diffusion length of charge carriers in Cu$_2$O restricted the thorough extraction of photoelectrons (Musselman et al., 2010). It has been demonstrated that various eye-of-sight deposition techniques can be used for the Cu$_2$O structure...
with minor curvatures to address these challenges (Paracchino et al., 2012; Minguez-Bacho et al., 2015), such as the thermal evaporation or e-beam deposition, providing a straightforward and effective solution to load diverse functional layers (Dubale et al., 2015; Han et al., 2015). The multilayered integration of desired components greatly enhances both the efficiency and stability of Cu2O photocathodes (Zhang et al., 2013; João et al., 2016). For instance, using the rationally designed Ga2O3/TiO2/RuO2 overlayer, the photocathode exhibited an unprecedented stable high internal quantum efficiency over 120 h (Pan et al., 2018).

On the other hand, in recent years, the morphology control of the p-type light-absorbing layer has been recognized as another answer to effectively balance the surface area and charge transport pathways (Chen et al., 2012; Concina et al., 2017). The state-of-the-art efficiency has been achieved by engineering Cu2O from flat films into nanowire arrays (NWAs) to facilitate photocarrier extraction (Qu et al., 2019). By incorporating the merit of all measures, the Cu2O NWA-based photocathodes were manifested as the landmark featuring their excellent photoelectrochemical (PEC) efficiency and stability (Huang et al., 2013). Unfortunately, these three-dimensional architectures also drastically increased the difficulty of the fabrication processes. Given the great curvatures and existing shaded area on NWAs, only atomic-layer deposition is capable of realizing the uniform heterojunctions with intimate contact of components (Luo et al., 2016). Undoubtedly, the realization of the desired coating is the key to fully eliciting the potential of the complicated nanostructures.

Specifically, titanium oxide appears to be one of the essential components in the coating. It does not only prevent corrosions of Cu2O from the electrolyte solution but also rectifies the flow of photogenerated carriers (Li et al., 2015). The heterojunction between Cu2O and titanium oxide via various techniques has been demonstrated as essential for these high-performance photocathodes (Siripala et al., 2003; Lumley et al., 2019). However, as we stated, there are only extremely limited approaches that can be used for Cu2O NWAs (and certainly for other p-type nanostructures). Besides, titanium oxide has other uses (Azvedo et al., 2016; Yang et al., 2018; Wang et al., 2021). The most well-established yet almost the only route without post-treatments, the atomic-layer deposition technique, demands sophisticated instrumentation with expensive precursors (organometallic complexes) and experienced selection of conditions that delivers great impacts to the properties of the coating (Dai et al., 2014). On the other hand, there are incompatibility issues during the chemical depositions, whereas many of the bare p-type structures are instable. For instance, the hydrolysis of Ti alkoxide forms uniform titania coatings but requires following high-temperature annealing for the crystallization, which may be destructive for the bottom nanostructures (Paracchino et al., 2011). Therefore, a facile and mild titanium oxide deposition method is highly desired.

Specifically, there is no ready-to-use and uniform coating of semiconductive titanium oxides on Cu2O NWAs via chemical room temperature chemical route yet (Jang and Lee, 2019). The chemical limitation in aqueous electrolytes has been suggested by the Pourbaix diagram of the Cu element (Yang et al., 2017). The compatible conditions for Cu2O are restricted to near-neutral solutions with a narrow redox potential range. Notably, many previously reported electrodeposition of titanium oxides in harsh pH and oxidative conditions are not applicable (Eisenberg et al., 2014), for instance, the cathodic coating using the peroxide-dissolved Ti complex or anodizing Ti3+ in the strongly acidic solution (Kavan et al., 1993; Matsumoto et al., 2000). Nonetheless, titanium oxide layers from oxidizing Ti(III) over other nanostructures effectively formed various junctions, exhibiting outstanding photochemical or PEC properties (Toe et al., 2019). Unfortunately, none of these electrochemical processes is applicable to Cu2O nanostructures.

In this work, we successfully developed a new electrochemical route to realize the coating of functional titania over Cu2O NWAs. Owing to the mild environment and the deliberately controlled transient anodization, the coating thickness can be regulated with the well-maintained original NWA morphology. More importantly, the great portion of Ti3+ in the structure directly endows the coating’s good charge extraction and transport ability. Specifically, the almost tripled photocurrent (from 1.17 to 3.07 mA/cm², 0.55 V vs. RHE) and the positive shift of onset potential of the Cu2O–TiOx NWA photocathodes clearly prove the formation of a heterojunction facilitating the directional flow of photoelectrons. Moreover, combining its functionality with the assistance of the HER catalyst further raises the activity of the photocathodes. These features of the photocathodes present a new promising route of using a rationally designed electrochemical process to fabricate uniform and functioning heterostructure under mild conditions.

RESULTS AND DISCUSSION

Figure 1 schematically illustrates the preparation process of the Cu2O/TiO2/Ni NW photocathodes. The bottom Cu2O NWAs were prepared by a two-step method using our previously reported anodization process for uniformed Cu(OH)2 NWAs, followed by a spontaneous thermal conversion to Cu2O in an inert atmosphere (Cao et al., 2020). Morphologies of the photocathode at different fabrication stages were shown in scanning electron microscope (SEM) graphs (Figures 2A–D). The process was initiated by preparing uniform high-density Cu(OH)2 NWAs, with an average length of approximately 9 µm. After annealing in N2, Cu(OH)2 was converted into Cu2O NWAs. As seen from Figure 2B, the transformed arrays consisted of twisted and slightly shortened nanowires with an average length of 6.8 µm. The typical obtained Cu2O/TiO2 NWAs are shown in Figure 2C. The thin layer of amorphous TiOx can barely be seen on the SEM micrograph, whereas some of the adjacent NWs were seized as bundles by the coating. The thickness of the TiOx layer was estimated using transmission electron microscope (TEM) (Figure 2E) and high-angle annular dark-field scanning transmission electron microscope/energy dispersive X-ray mapping (Figure 2H) as approximately 30–50 nm. The aspect ratio slightly decreased but still could provide shortened diffusion
paths for the photoelectron to the solid-electrolyte interface than the flat structures. Eventually, a thin layer (~3 nm) of Ni was deposited onto the structure as the hydrogen evolution reaction (HER) catalyst, with no evident morphological impact (Figure 2D).

The nature of the electrodeposited titanium oxide coating layer was revealed by TEM microscopy. Figure 2E shows the typical structure of Cu$_2$O/TiO$_x$ core-shell NWs in the array, clearly showing that Cu$_2$O NWs were encapsulated by an amorphous layer. The titania layer was approximately 40 nm thick and assembled by primary clusters smaller than 5 nm. Micrographs showed intimate contacts of this coating layer with the inner Cu$_2$O NW. A minor porosity and notable roughness can be found as well. The selected area electron...
diffraction pattern (Figure 2F) only exhibited rings corresponding to (111), (200), (220), and (311) d-spacing of Cu₂O, suggesting its polycrystalline nature. No evidence of crystallized titanium oxides was observed either, which agrees with the X-ray diffraction (XRD) result (Figure 3A). High-angle annular dark-field scanning transmission electron microscope/energy dispersive X-ray mapping (Figure 2H) illustrates the elemental distribution line profile and mapping across a typical NW. The signal of oxygen sketches the overall shape of the NW, whereas Cu and Ti panels clearly confirm the spatial relationship of a core-shell structure.

The phase composition of the heterostructure was confirmed by XRD as well (Figure 3A). Despite the diffraction of 43.3 and 50.4° corresponding to (111) and (200) d-spacing of metallic Cu substrate (JCPDS 58-1326), respectively, all other peaks can be indexed to the pattern of cubic Cu₂O (JCPDS 75-1531). No other diffraction peaks were found on the XRD pattern, suggesting the TiOₓ layer was amorphous. Raman spectroscopy was used to further study the composition regarding the existence of amorphous oxides. Figure 3B shows the Raman spectra of Cu₂O and Cu₂O/TiOₓ samples. Common features on both spectra at 109, 148, 416, 515, and 635 cm⁻¹ can be assigned to the vibrational modes of Cu₂O lattices (Maldonado-Larios et al., 2018). Different from the XRD technique, TiOₓ (amorphous) on Cu₂O/TiOₓ sample are associated with the deformation of out-of-plane rings (Ohsaka et al., 1978; Jumat et al., 2017). Given that no other peaks were observed, the Raman spectroscopy strongly supported the existence of titania as an amorphous form. Moreover, the successful coating was further confirmed by the ultraviolet–visible diffuse reflectance spectroscopy of Cu₂O NWAs and Cu₂O/TiOₓ NWAs samples (Supplementary Figure S1). The latter had much stronger light absorption in ultraviolet, indicating the deposition of the TiOₓ layer over the entire sample. The absorption in the visible range slightly decreased (in K-M expression), which is likely due to the increased scattering. Nonetheless, from the view of PEC efficiency, this is negligible on the scale of the reflection rates (Supplementary Figure S1).

X-ray photoelectron spectroscopy survey was carried out to collect the valence state and chemical environment information of elements in the Cu₂O/TiOₓ photocathode. The full spectral range scans (Supplementary Figure S2) confirmed the elemental composition of Cu, O, and Ti. The fine scan of the Ti 2p spectrum (Figure 3C) shows the typical bands of Ti 2p½ and Ti 2p½ core levels at 458.5 and 464.9 eV, respectively. The experimental curves were well fitted with the Gaussian peaks model after Tougaard background subtraction, whereas the valence states of Ti can be identified by deconvoluting the fitting result, consisting of both Ti³⁺ and Ti⁴⁺. To our surprise, the percentage of Ti³⁺ is as high as 38% in the coating layer (Supplementary Table S1). The signal from O 1s is slightly more complicated (Figure 3D), showing three different chemical environments: metal oxides (Ti-O at 529.1 and Cu-O 530.7 eV), hydroxyl (535.6 eV), and absorbed water (532.3 eV). Because the sample was not annealed, the carboxylic group should be the result of residue oxalate in the electrolyte. It is worthy to note that the signal from Cu in Cu₂O is stronger and higher than the expectation of having a screening effect from the titania shell. According to TEM (Figures 2E–G), this could be from the recrystallized small Cu₂O clusters during the deposition process. In short, the X-ray photoelectron spectroscopy result confirms the overall composition of the sample as oxides, but the coating layer cannot be simply regarded as TiO₂, given its extremely high level of Ti³⁺. On the other hand, apparently, the coating does not contain a large number of hydroxyl groups. This can be beneficial to charge transport by reducing the chance of recombination (Carp et al., 2004).

The structural analysis discussed earlier proved the realization of our electrochemical route. Chemical compatibility is the essential challenge in this deposition process. Given the vulnerability of Cu₂O, the electrolyte solution has to be near neutral. On the other side, Ti³⁺ is unstable as well, which hydrolyzes when pH > 4 and can be easily oxidized into hydrated TiO₂ (Johnson et al., 2017). Hence, all reported cases were performed under very low pH with relatively stable substrates. We took several measures to stabilize Ti³⁺ and bring it to a workable condition for Cu₂O. A water/ethylene glycol solution was used instead of a typical pure aqueous system. Hydrolysis of Ti(III) can be notably reduced with the interaction between high valent ions with the polylol environment. An optimal composition was experimentally determined as 50% (Supplementary Figure S3). Chelating/complex agents were introduced to further stabilize Ti(III) species (Lavacchi et al., 2021). The oxalic acid was selected based on both the coating coverage and photocurrent of the product.
Different electrochemical techniques were considered as well. Ideally, the electrodeposition can be performed using various techniques, such as the galvanostatic or potentiostatic process, or transient methods such as linear potential scans or AC controls. However, as we tested, none of the galvanostatic or potentiostatic processes produced reliable and reproducible results. This could be due to the large surface conductivity change during the deposition. On the contrary, directly using the LSV scan worked quite well for the deposition. In addition, the scan rate can be used as a handy tool to kinetically discriminate reactions, which reduces the redox corrosion to Cu₂O. In our case, severe destruction to the NWA structure or insufficient deposition was observed with inappropriate scan rates (Supplementary Figure S6).

Moreover, fine control of the thickness of TiOₓ can be achieved by regulating the anodization charge during the deposition process (Figure 4). Figure 4A shows the typical relatively smooth surface of the pristine Cu₂O structures before the deposition of TiOₓ. After that, as the anodization progressed, amorphous TiOₓ was gradually loaded onto the Cu₂O surface (Figures 4B–D) with increasing amounts. At the anodic charge of 0.5 C cm⁻² (Figure 4B), the Cu₂O surface was roughened with the discrete coating of approximately 10 nm, which is not sufficient to completely hinder the photo-corrosion of Cu₂O yet. Meanwhile, a minor improvement to the photocurrent was observed (Supplementary Figure S7). As the charge increased to 0.9 C cm⁻², more amorphous TiOₓ was loaded onto Cu₂O, whereas the thickness was measured as approximately 20 nm (Figure 4C). In the finishing stage, the Cu₂O NWs were fully covered by the deposited TiOₓ layer, with the coating thickness eventually reaching 40 nm (Figure 4D). The complete deposition notably improved water reduction photocurrents of the NWA photocathode from 1.35 to 4.15 mA/cm² at 0.55 V vs. RHE (Supplementary Figure S7). In principle, further thicker coating might be possible by optimizing conditions. However, for our current purpose in the PEC application, coating less than 50 nm is reasonable and similar to the typical thickness of reported titanium oxide layers (Musselman et al., 2010).

The PEC performance confirmed the functionality of the coating layer, as shown in Figure 5. Specifically, LSV scans of pristine-Cu₂O, Cu₂O/TiOₓ, and Cu₂O/TiOₓ/Ni photocathodes were collected in 0.5-M sodium phosphate buffer under chopping AM1.5G illumination. The current density–potential curves clearly show that Cu₂O/TiOₓ photocathode had a significantly enhanced photoactivity, in which photocurrent density reached ~3.0 mA/cm² at 0.55 V vs. RHE, whereas the pristine-Cu₂O only had ~1.1 mA/cm² parallely. Moreover, with Ni cocatalyst loaded onto Cu₂O/TiOₓ photocathodes, the photocurrent density could be further enhanced to ~4.7 mA/cm² at 0.55 V vs. RHE, which is over four times higher than that of pristine Cu₂O photocathode, showing a significant enhancement in photo-response that resulted from the effective heterojunction formed inside of Cu₂O/TiOₓ. Furthermore, Cu₂O/TiOₓ/Ni photocathode had a more positive onset potential of 0.82 V vs. RHE, 0.18 V positive to the Cu₂O photocathode, as shown in Figure 5A. Both of these phenomena indicate that the Cu₂O/TiOₓ/Ni interface could

![Figure 4](https://example.com/figure4.png)

**Figure 4** | Chronology of TiOₓ formation in potentiodynamic anodization process: (A) Scanning electron micrographs of bare Cu₂O NWAs; (B–D) Corresponding scanning electron microscope images showing morphological evolution of amorphous TiOₓ along with increasing anodization charge. (E) Typical LSV curve of anodizing a piece of Cu₂O foil with rate of 5 mV/s, data points labeled with charges specifying samples examined in parts b–d and (F) schematic model to formation of Cu₂O/TiOₓ/ NWAs.
significantly improve the utilization of photocarriers with the smaller hindrance and the lower activation energy barrier in comparison with the pristine Cu$_2$O surface.

As is shown in Figure 5B, the TiO$_x$ coating and Ni cocatalyst notably benefited the stability of the photocathodes. The photocurrent of pristine-Cu$_2$O photocathode decreased by approximately 60% in 40 min. SEM (Supplementary Figure S8) image as pieces of evidence that the NWs were seriously damaged and deformed. Energy dispersive X-ray (EDX) analysis confirms the decrease of oxygen content, indicating that the Cu$_2$O was considerably reduced. This agrees with the typical photo-corrosion mechanism of Cu$_2$O (Toe et al., 2019). With the coating of the TiO$_x$ layer, the stability of the photocathode was notably improved. The photocurrent density decreased by approximately 40%. It is reasonable to speculate that it was still due to the self-reduction reaction, according to the EDX result. Metallic Cu nanoparticles can be distinctly discriminated after the test (Supplementary Figure S8D), implying the leakage of Cu to the electrolyte. Furthermore, the location of the speculated Cu islands indicates that the photoelectrons have been extracted to the TiO$_x$ part. Otherwise, the reduction of Cu$_2$O should not produce Cu crystallites outside the coating. Nonetheless, HER was not the favored reaction over the surface due to lacking HER sites. Once the necessary catalyst (Ni) was integrated, the photocathodes became much more stable with better PEC efficiency. SEM and EDX (Supplementary Table S2) confirmed that the morphology and composition of Cu$_2$O/TiO$_x$/Ni photocathode were well maintained after the stability test. Only very few bright metallic Cu islands can be found on the surface of the photocathode, which validated the functionality of the cocatalyst. It is worthy to emphasize that the coating of this single TiO$_x$ layer is helpful for the photoelectron collection from Cu$_2$O but still not the ultimate solution to the system. Clearly, an additional measure is necessary to fill out the pores, and the efficiency of the photocathodes can be further improved. Nonetheless, the deposition of TiO$_x$ solved one of the most important yet challenging steps for the functionalization of Cu$_2$O.

The key advantage of the nanostructure approach is the ability to improve the charge transport and minimize the recombination by constructing heterojunction and providing a stable support structure for the cocatalyst. The incident photon-to-current efficiency (IPCE) obtained from the LSV measurement was greatly improved. As shown in Figure 5C, the IPCE for the Cu$_2$O/TiO$_x$/Ni photocathode is reasonably higher than that of the pristine-Cu$_2$O across the whole wavelengths, especially in the visible region between 420 and 470 nm.

To understand the details of the charge transfer in the photocathodes, we performed an electrochemical impedance spectroscopy (EIS) study, which is a powerful frequency domain analysis technique for investigating electrical characters of interfaces (Chen et al., 2017). Figure 6A shows the impedance data of parallelly tested samples with complex coordinates as Nyquist plots. The very high-frequency region on the lower left corresponds to the series resistance and response from the counter electrode, which is approximately 5 $\Omega$ for all samples. Semicircles on the plots represent the impedance of interfaces or electrochemical processes, whereas the diameters of semicircles are equal to the corresponding resistances. Straightforwardly, a larger semicircle correlates to worse charge transportation through that interface. The linear portion of the lower frequency, so-called a Warburg element, represents the diffusion-controlled impedance (Kecsenovity et al., 2017). Visually, the charge transfer difference of Cu$_2$O, Cu$_2$O/TiO$_x$, and Cu$_2$O/TiO$_x$/Ni photocathodes can be clearly addressed in the plots (Figure 6A). The step-by-step architecting by the TiO$_x$ coating and cocatalyst loading gradually lowered the overall charge transport impedance. The fitting result (Supplementary Table S3) indicates that the Cu$_2$O/TiO$_x$ samples have a much smaller $R_{ct}$ in comparison with pristine-Cu$_2$O, which benefits from the promoted charge separation and transport under the assistance of the Cu$_2$O–TiO$_x$ heterojunction. Meanwhile, $CPE1$ has increased several times, implying a capacitive feature on the Cu$_2$O–TiO$_x$ interface. All interfacial resistances were further reduced by Ni cocatalyst loading. Particularly, $CPE2$ is notably smaller, suggesting less charge accumulation on the photocathodes because of the expedited HER pathway.

Figures 7A–C show the Mott–Schottky (M–S) measurement results of the photocathodes. The measurement can be used to determine the type of semiconductors, flat band potentials, and carrier densities (Patel et al., 2017; Sivula, 2021). Using the
following equation, important semiconductor parameters were linked together:

\[ \frac{1}{C_{SC}} = \frac{2}{\varepsilon N e_0 A^2} \left( V - V_{fb} \right) - \frac{T k_B}{e} \]

where \( C_{SC} \) is the space-charge capacitance, \( V \) is the applied potential, \( V_{fb} \) is the flat band potential, \( \varepsilon \) is the dielectric constant of \( \text{Cu}_2\text{O} \), \( e_0 \) is the permittivity of vacuum, \( A \) is the area, \( N \) is the carrier density, \( e \) is the electron charge, \( k_B \) is the Boltzmann’s constant, and \( T \) is the absolute temperature.

According to the equation discussed earlier, intercepts of the curve in M-S plots were used to determine \( V_{fb} \). For the \( \text{TiO}_x \) (Supplementary Figure S9) on metal and the bared \( \text{Cu}_2\text{O} \) NWA (Figure 7A), a relatively straightforward result can be obtained indicating their n-type and p-type semiconductive nature, respectively. However, in the case of the possible frequency dispersion caused by nonideal behaviors of electrode capacitances, their M-S correlations were plotted using a series of frequencies. The dataset suggests the \( V_{fb} \) of the \( \text{Cu}_2\text{O} \) photocathode as 0.78 V vs. RHE. For \( \text{Cu}_2\text{O}/\text{TiO}_x \) and \( \text{Cu}_2\text{O}/\text{TiO}_x/\text{Ni} \) photocathodes, large frequency dispersion was observed. A precise determination of their flat band potentials is unrealistic, although their \( V_{fb} \) can be speculated to be similar to pristine-\( \text{Cu}_2\text{O} \) or with minor positive shifts. On the other hand, the measurements manifest the carrier density difference between the three electrodes. Specifically, the reciprocal of slopes on the tangents are proportional to \( N \), the carrier densities in the space charge region. Despite the frequency dispersion, the slopes of \( \text{Cu}_2\text{O}/\text{TiO}_x \) are an order smaller than pristine-\( \text{Cu}_2\text{O} \), suggesting more responding charge carriers in the space charge region. This increment hints at a more efficient extraction.
of photoelectrons and less recombination in the bulk. According to the structure of the photocathodes, this beneficial effect shall be attributed to the electric field formed on the heterojunction interface, which alters the carrier distribution in Cu$_2$O and subsequently notably facilitates the carrier extraction.

CONCLUSION

In short, we successfully achieved the aimed titanium electrodeposition in near-neutral conditions for preparing uniform heterojunction over a vulnerable p-type semiconductor nanostructure. Due to the existence of a large portion of Ti$^{3+}$, this electrodeposited layer directly exhibited a charge transport ability without any post-treatment. Both the onset potential and PEC efficiency of the NWA photocathodes were greatly improved. By further incorporating with Ni-based HER cocatalyst, the accomplished photocathodes exhibited a photocurrent approximately four times of the pristine-Cu$_2$O NWAs, with a much longer lifetime. Electrochemical impedance spectroscopy and M-S measurements revealed that the TiO$_2$ layer facilitated the charge transport inside the space charge region. This protocol is reliable and effective but requires no sophisticated instrumentation. These merits make it easily applicable to other unstable nanostructures. Moreover, these results demonstrated the possibility of electrochemically fabricating cost-effective photoelectrodes with both earth-abundant materials and affordable preparation expenditures.

REFERENCES

Azevedo, J., Tilley, S. D., Schreier, M., Stefk, M., Sousa, C., Aratijo, J. P., et al. (2016). Tin Oxide as Stable Protective Layer for Composite Cuprous Oxide Water-Splitting Photocathodes. 

Nano Energy 24, 10–16. doi:10.1016/j.nanoen.2016.03.022

Cao, Y., Liu, D., Ni, X., Meng, X., Zhou, Y., Sun, Z., et al. (2020). Better Charge Separation in CuO Nanowire Array Photocathodes: Micro-nanostructure Regulation for Photoelectrochemical Reaction. 

ACS Appl. Energ. Mater. 3, 6334–6343. doi:10.1021/acsenermlett.0c00554

Carp, O., Huismann, C. L., and Reller, A. (2004). Photoinduced Reactivity of Titanium Dioxide. 

Prog. Solid State. Chem. 32, 33–177. doi:10.1016/j.psschem.2004.08.001

Chen, H. M., Chen, C. K., Liu, R.-S., Zhang, L., Zhang, J., and Wilkinson, D. P. (2012). Nano-Architecture and Material Designs for Water Splitting Photocathodes. 

Chem. Soc. Rev. 41, 5654–5671. doi:10.1039/C2CS35019F

Chen, W., Zhang, W., Chen, L., Zeng, L., and Wei, M. (2017). Facile Synthesis of CuO Nanorod Arrays on Cu Foam as a Self-Supporting Anode Material for Lithium Ion Batteries. 

J. Alloys Compd. 723, 172–178. doi:10.1016/j.jallcom.2017.06.153

Concina, I., Iupoto, Z. H., and Vomiero, A. (2017). Semiconducting Metal Oxide Nanostructures for Water Splitting and Photovoltaics. 

Adv. Energ. Mater. 7, 1700706. doi:10.1002/aenm.201700706

Dai, P., Li, W., Xie, J., He, Y., Thorne, J., Mcmahon, G., et al. (2014). Forming Buried Junctions to Enhance the Photovoltage Generated by Cuprous Oxide in Aqueous Solutions. 

Angew. Chem. Int. Ed. 53, 13493–13497. doi:10.1002/anie.201408375

Dubale, A. A., Pan, C.-J., Tamirat, A. G., Chen, H.-M., Su, W.-N., Chen, C.-H., et al. (2015). Heterostructured Cu$_2$O/CuO Decorated with Nickel as a Highly Efficient Photocathode for Photoelectrochemical Water Reduction. 

J. Mater. Chem. A. 3, 12482–12499. doi:10.1039/c5ta01961c

Eisenberg, D., Ahn, H. S., and Bard, A. J. (2014). Enhanced Photoelectrochemical Water Oxidation on Bismuth Vanadate by Electrodeposition of Amorphous Titanium Dioxide. 

J. Am. Chem. Soc. 136, 14011–14014. doi:10.1021/ja5082475

Han, J., Zong, X., Zhou, X., and Li, C. (2015). Cu$_2$O/CuO Photocathode with Improved Stability for Photoelectrochemical Water Reduction. 

RSC Adv. 5, 10790–10794. doi:10.1039/c4ra13896a

Huang, Q., Kang, F., Liu, H., Li, Q., and Xiao, X. (2013). Highly Aligned Cu$_2$O/Cu$_2$O/TiO$_2$core/shell Nanowire Arrays as Photocathodes for Water Photoelectrolysis. 

J. Mater. Chem. A. 1, 2418–2425. doi:10.1039/c2ta00918h

Jang, Y. J., and Lee, J. S. (2019). Photoelectrochemical Water Splitting with p-Type Metal Oxide Semiconductor Photocathodes. 

ChemSusChem 12, 1835–1845. doi:10.1002/cssc.201802596

Johnson, K. E., Gakhar, S., Deng, Y., Fong, K., Rübsud, S. H., and Longo, M. L. (2017). Biomembrane-Compatible Sol-Gel-Derived Photoelectrocatalytic Titanium Dioxide. 

ACS Appl. Mater. Inter. 9, 35664–35672. doi:10.1021/acsami.7b12673

Junat, N. A., Wai, P. S., Ching, J. J., and Basirun, W. J. (2017). Synthesis of Polyallamine-TiO$_2$ Nanocomposites and Their Application in Photocatalytic Degradation. 

Polym. Polym. Compos. 25, 507–514. doi:10.1177/096739191702500701

Kavan, L., O’Regan, B., Kay, A., and Grätzel, M. (1993). Preparation of TiO$_2$ (Anatase) Films on Electrodes by Anodic Oxidative Hydrolysis of TiCl$_4$. 

J. Electroanal. Chem. 346, 291–307. doi:10.1016/0022-0728(93)85020-H

Kecsenovity, E., Endrődi, B., Tóth, P. S., Zou, Y., Dyle, R. A. W., Rajeshwar, K., et al. (2017). Enhanced Photoelectrochemical Performance of Cuprous Oxide/Gaphene Nanohybrids. 

J. Am. Chem. Soc. 139, 6682–6692. doi:10.1021/jacs.7b01820

Lavacchi, A., Bellini, M., Berretti, E., Chen, Y., Marchionni, A., Miller, H. A., et al. (2021). Titanium Dioxide Nanomaterials in Electrocatalysis for Energy. 

Carr. Opin. Electrochern. 28, 100720. doi:10.1016/j.joc.2021.100720

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

YC conceived and designed the experiments. HQ assisted in experiments and the revision process. YLZ analyzed experimental data and modified articles, and NA, and YZ modified articles. All authors contributed to the article and approved the submitted version.

FUNDING

This work was supported by the National Natural Science Foundation of China (grant nos. 21805298 and 21905288), Ningbo’s major special projects of the Plan “Science and Technology Innovation 2025” (no. 2018B10056), and Ningbo 3315 Program.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.832342/full#supplementary-material

Efficient Photocathode for Photoelectrochemical Water Reduction. 

J. Mater. Chem. A. 3, 12482–12499. doi:10.1039/c5ta01961c
Li, C., Hisatomi, T., Watanabe, O., Nakabayashi, M., Shibata, N., Domen, K., et al. (2015). Positive Oscillator Potential and Stability of Cu2O-Based Photocathodes in Water Splitting by Atomic Layer Deposition of Cu2S on Ca2O Buffer Layer. Energy Environ. Sci., 8, 1493–1500. doi:10.1039/c5ee00250h

Li, C., He, J., Xiao, Y., Li, Y., and Delaunay, J.-J. (2020). Earth-abundant Cu-Based Metal Oxide Photocathodes for Photoelectrochemical Water Splitting. Energy Environ. Sci., 13, 3269–3306. doi:10.1039/D0EE02397C

Liu, Z., Wang, L., Li, L., Qiu, F., Xiong, X., Tao, C., et al. (2020). Surfactant Effect on Controllable Phase Transformation and UV-Shielding Performance of Titanium Dioxide. Mater. Chem. Phys., 240, 122079. doi:10.1016/j.matchemphys.2019.122079

Lumley, M. A., Radmilovic, A., Jan, Y. J., Lindberg, A. E., and Choi, K.-S. (2019). Perspectives on the Development of Oxide-Based Photocathodes for Solar Fuel Production. J. Am. Chem. Soc., 141, 18358–18369. doi:10.1021/jacs.9b07976

Luo, J., Steier, L., Son, M.-K., Schreier, M., Mayer, M. T., and Grätzel, M. (2016). Cu2O Nanowire Photocathodes for Efficient and Durable Solar Water Splitting. Nano Lett., 16, 1848–1857. doi:10.1021/acs.nanolett.5b04929

Maldonado-Larios, L., Mayen-Mondragon, R., Martinez-Orozco, R. D., Paramo-Garcia, U., Gallardo-Rivas, N. V., and Garcia-Alamilla, R. (2020). Electrochemically-assisted Fabrication of Titanium-Dioxide/polyaniline Nanocomposite Films for the Electrocatalysis of Tungsten Carbide in Aqueous Solvents. Synth. Met., 268, 116464. doi:10.1016/j.synthmet.2020.116464

Matsumoto, Y., Ishikawa, Y., Nishida, M., Li, S., Wang, G., and Li, Y. (2000). A New Active Oxide Photocathode for Photoelectrochemical Water Reduction. Adv. Funct. Mater., 24, 303–311. doi:10.1002/adfm.201301106

Toe, C. Y., Scott, J., Amal, R., and Ng, Y. H. (2019). Recent Advances in Suppressing the Photocorrosion of Cuprous Oxide for Photocatalytic and Photoelectrochemical Energy Conversion. J. Photochem. Photobiol. C: Photochem. Rev., 40, 191–211. doi:10.1016/j.jphotochemrev.2018.10.001

Wang, S., Yu, W., Xu, S., Han, K., and Wang, F. (2021). Ammonia from Photothermal N2 Hydrogenation over NiTiO3 Catalysts under Mild Conditions. ACS Sustain. Chem. Eng., 10, 115–123. doi:10.1021/acssuschemeng.1c04931

Wick, R., Tilley, S. D. (2015). Photovoltaic and Photoelectrochemical Solar Energy Conversion with Cu2O. J. Phys. Chem. C, 119, 26243–26257. doi:10.1021/acs.jpcc.5b08397

Yang, Y., Niu, S., Han, D., Liu, T., Wang, G., and Li, Y. (2017). Progress in Developing Metal Oxide Nanomaterials for Photoelectrochemical Water Splitting. Adv. Energ. Mater., 7, 1700555. doi:10.1002/aenm.201700555

Yang, J., Du, C., Wen, Y., Zhang, Z., Cho, K., Chen, R., et al. (2018). Enhanced Photoelectrochemical Hydrogen Evolution at P-type CuBi2O4 Photocathode through Hypoxic Calcination. Int. J. Hydrogen Energ., 43, 9549–9557. doi:10.1016/j.ijhydene.2018.04.066

Zhang, Z., Dua, R., Zheng, L., Zhu, H., Zhang, H., and Wang, P. (2013). Carbon-layer-protected Cuprous Oxide Nanowire Arrays for Efficient Water Reduction. ACS Nano, 7, 1709–1717. doi:10.1021/nn3057092

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher’s Note: All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations or those of the publisher, the editors, and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.