

Supplementary Material

Experimental

All chemicals used in this study were analytical grades and used without further purification. The copper foil (99.9%, 1.0 mm thick, 1×1 cm²) was cleaned with acetone, ethanol and deionized water in turn.

(1) Preparation of Cu₂O NWA Photocathodes

The copper foil was anodized in an electrochemical cell with a typical standard three-electrode setup, using an alkali solution (3 M KOH and 0.07 M cetyltrimethylammonium bromide (CTAB)) to form $Cu(OH)_2/Cu$ NWAs foil. The Cu_2O/Cu foil formed by a thermal treatment which was carried out with a heating ramp of 5 °C min⁻¹ and maintained at 350 °C for 1 h in N₂ atmosphere. Afterward, the samples were left to cool naturally to room temperature and then collected for further treatment.

(2) Preparation of Cu₂O/TiO_x NWA Photocathodes

The Cu₂O/TiO_x NWA Photocathodes were prepared by potentiodynamic anodization with the threeelectrode configuration (a Pt wire as the counter electrode and Ag/AgCl as the reference electrode). The electrolyte solution was made of 1.26 g oxalic acid, 2.5 mL TiCl₃ (18%), 50 mL ethylene glycol and 50 mL of deionized water, with pH adjusted to 6 by 1 M NaHCO₃ solution. The potential of the work electrodes (Cu₂O NWA) was anodically scanned from -0.25 to 0.75 V (vs Ag/AgCl) at 5 mV/s. Afterwards, the Cu₂O/TiO_x photocathodes were rinsed with DI water and dried in the desiccator at room temperature.

(3) Preparation of Cu₂O/TiO_x/Ni Composite Photocathode

A layer of Ni with a thickness of 3 nm was deposited on the Cu_2O/TiO_x NWA samples by thermal evaporation to act as a co-catalyst for hydrogenation.

Photoelectrochemical and Electrochemical Impedance Measurements

Photoelectrochemical measurements were carried out on CHI-600D in a three-electrode configuration, with samples as the working electrode, a Pt wire as CE and Ag/AgCl/saturated-KCl as RE. 0.5 M aqueous phosphate solution (pH 6.0) was used as the electrolyte. In typical photocurrent tests with the Linear Sweep Voltammetry (LSV), a cathodic 5 mV/s scan was used with AM1.5G illumination (100 mW/cm²) chopped every 5 s. The electrochemical impedance spectroscopy (EIS) measurement was carried out using the same apparatus and recorded by a Modulab-XM Solartron potentiostat using multi-sine mode and 455 nm LED (39 mW/cm²). The frequency ranges were measured from 1 MHz to 1 Hz with a sinusoidal potential perturbation of 10 mV with zero bias to the open circuit potentials of the samples. The Mott–Schottky plots were extracted from the datasets of staircase-potential EIS measurements covered the varied potential and frequencies.

Instrumentation

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The morphologies of samples were recorded by the Scanning Electron Microscope (FEI Quanta FEG 250 and Hitachi S-4800 equipped with TLD) and TEM (Tecnai F20). The chemical composition was determined by the SEM integrated Energy Dispersive Spectrometer (EDS). XRD patterns were acquired with a Bruker D8 ADVANCE DAVINCI X-ray diffractometer (Cu K α 1, 40 kV / 200 mA). The X-ray photoelectron spectroscopy (XPS) data was collected using a PHI Quantum 2000 XPS system (Al K α source) and calibrated with adventitious C1s signal. The UV–vis Diffuse Reflectance Spectra (UV–vis DRS) were recorded with PerkinElmer Lambda 950 spectrophotometer using a Teflon microbeads reference. Raman spectra were collected using a Renishaw Raman system with Ar (532.8 nm) laser excitation.



Fig. S1. Reflection spectra derived from diffuse reflectance via Kubelka-Munk theory.



Fig. S2. XPS broad scan spectra of the typical Cu₂O/TiO_x NWA sample.

Area(%)	Fwhm	Position
57698.3 (61.38)	2.58	458.9
	2.37	464.6
36305.2 (38.62)	2.17	457.8
	2.13	462.8
Area	Fwhm	Position
99868.2	2.30	530.7
2946.0	1.81	532.3
48626.8	1.93	533.4
24674.9	1.80	529.1
9070.8	4.40	535.6

Table S1. XPS data fitting result details of Ti2p and O1s core levels.



Fig. S3. Impacts of the ratio of deionized water (DI) to glycol (GR) in the anodization electrolyte solution: SEM images of Cu₂O/TiO_x NWAs prepared in (a) DI:GR=2:3, (b) DI:GR=1:1, (c) DI:GR=3:2 (d-f) enlarged images of their left images, respectively, (g) apparent surface oxygen, copper, and titanium to carbon atom ratios of anodized samples (calculated from SEM-EDS) and (h) the PEC-LSV scan (5 mV s⁻¹) curves performed in a 0.5 M potassium phosphate buffer at pH=6.0, under 36 mW cm⁻² 455 nm LED illumination chopped every 5 s.

All of the following photocurrent and voltage (PEC-LSV) test conditions are identical and unless further specified.



Fig. S4. Impacts of the presence or absence of surfactants (Triton X-100) in the anodization electrolyte solution: SEM images of Cu_2O/TiO_x (a) presence and (b) absence of 1 mM surfactants during the anodized deposition of TiO_x system respectively; (c)Apparent surface oxygen, copper, and titanium to carbon atom ratios of anodized samples (calculated from SEM-EDS) and (h) the PEC test of a group samples under the corresponding conditions, using default procedures as above with 455 nm blue LED.



Fig. S5. Impacts of temperature of TiO_x deposition in the anodization electrolyte solution: SEM images of Cu₂O/TiO_x NWAs prepared in (a) 15°C, (b) 25°C, (c) 35°C and (d) the PEC test of the samples under the corresponding conditions, using default procedures as above with 455 nm blue LED.



Fig. S6. Scan rate dependence of TiO₂ formation in the potentiodynamic anodization process: (a) SEM images of bare Cu₂O NWAs; Corresponding SEM images showing the morphological evolution of amorphous TiO_x along the increasing anodization scan rate (b) 1 mV/s, (c) 3 mV/s, (d) 5 mV/s, (e) 10 mV/s and (f) 50mV/s. (g) Apparent surface oxygen, copper, and titanium to carbon atom ratios of anodized samples (calculated from SEM-EDS) and (h) the PEC test of a group samples.



Fig. S7. Effect of the anodization charge to the TiO_x coating as controlled by stopping the anodization deposition under the default anodization rate (5mV/s).



Fig. S8. SEM images of samples before and after photoelectrochemical stability testing Cu₂O-based with different photocathodes (a-c) Cu₂O, Cu₂O/TiO_x and Cu₂O/TiO_x/Ni before testing; (d-f) Cu₂O, Cu₂O/TiO_x and Cu₂O/TiO_x/Ni after testing.

Table S2. Apparent surface oxygen, copper, and titanium to carbon atom ratios of samples before and after photoelectrochemical stability testing with the different Cu_kO -based photocathodes (calculated from SEM-EDS).

	Cu ₂ O		Cu ₂ O/TiO _x		Cu ₂ O/TiO _x /Ni	
Atomic %	before	after	before	after	before	after
Cu	71.9	76.6	59.81	61.08	58.50	59.45
0	28.1	23.4	37.85	36.73	38.01	37.63
Ti	-	-	2.34	2.19	2.65	2.21
Ni	-	-	-	-	0.84	0.71

parameter	Cu ₂ O	Cu ₂ O/TiO _x	Cu ₂ O/TiO _x /NiO _x
$R_{ss}(\Omega)$	5.708	4.884	3.202
$R_{ct1}(\Omega)$	6.583	5.015	4.069
W_{s} -R (Ω)	3.231	3.621	4.250
W _s -T (x10 ⁻³ F cm ⁻²)	1.010	3.501	10.10
CPE1-T (x10 ⁻³ F cm ⁻²)	1.454	5.261	2.332
CPE1-P	0.61	0.49	0.50
$R_{ct2}(\Omega)$	46.52	11.07	8.501
CPE2-T (x10 ⁻³ F cm ⁻²)	132.50	110.11	70.53
CPE2-P	0.78	0.81	0.97

Table S3. Model Parameters of the EIS Results (Figure 6a).



Fig. S9. M-S measurement of pure TiO_x layer on a nickel foam showing its n-type semiconductive feature (performed in a 0.5 M sodium sulfate solution, using the typical 3-electrodes configuration).