

*Electronic Supplementary Information (ESI)*

**Cu<sub>2</sub>O/NiO<sub>x</sub> nanocomposite as an inexpensive photocathode  
for photoelectrochemical water splitting**

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## Experimental Section.

**General considerations.** Starting materials for the synthetic part of the work were purchased from commercial suppliers and used as received, unless otherwise noted. All chemicals used for the analytical part were of the highest available purity. F-doped tin oxide (FTO) coated glass (sheet resistance  $7 \text{ ohm sq}^{-1}$ , TEC Glass<sup>TM</sup> 7) was kindly provided from Pilkington Group Limited, UK.

**Preparation of a Cu|*nano*Cu<sub>2</sub>O electrode.** This electrode consists of Cu<sub>2</sub>O nanowires (*nano*Cu<sub>2</sub>O wires) on a Cu foil. The Cu foil ( $1.0 \times 3.0 \text{ cm}^2$ , 1.27 mm in thickness, 99.9%; Alfa Aesar) was polished and cleaned in HCl solution (0.4 M) under ultrasonication. Subsequently, *nano*Cu(OH)<sub>2</sub> wires were grown on  $1.5 \text{ cm}^2$  of the Cu foil with epoxy tape (0.14 mm in thickness; 3M<sup>TM</sup>) as spacer by using chemical bath deposition from a solution containing 0.133 M ammonium persulfate (99.1%; Fisher Scientific) and 3.33 M NaOH (analytic grade; Breckland Scientific Supplies) at room temperature for 20 min,<sup>1</sup> followed by thermal conversion of *nano*Cu(OH)<sub>2</sub> wires to *nano*Cu<sub>2</sub>O wires under a N<sub>2</sub> atmosphere at 500 °C for 4 h.

**Preparation of a Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> electrode.** This electrode consists of NiO<sub>x</sub> deposited on Cu|*nano*Cu<sub>2</sub>O. A precursor solution (0.1 mL) containing 0.5 M nickel acetate tetrahydrate (98%, Alfa Aesar) and 0.5 M ethanolamine (99%; Sigma-Aldrich) in 2-methoxyethanol (99.5%; Sigma-Aldrich) was prepared and then spin-coated on the Cu|*nano*Cu<sub>2</sub>O electrode (geometrical surface area of  $1.5 \text{ cm}^2$ ) with 2,000 rpm for 10 s, followed by annealing in air at 200 °C with a Carbolite<sup>®</sup> furnace for 30 min. The film thickness of the NiO<sub>x</sub> layer on the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> electrode was tuned by repeating this procedure for several times.

**Preparation of a FTO|*nano*WO<sub>3</sub> electrode.** The FTO|*nano*WO<sub>3</sub> electrode contains WO<sub>3</sub> nanosheets deposited on FTO-coated glass and it was synthesized following a slight modification of a published procedure.<sup>2</sup> A precursor solution containing 0.625 g H<sub>2</sub>WO<sub>4</sub> (99%; Alfa Aesar), 0.5 g polyvinyl alcohol (98-99%, medium molecular weight; Alfa Aesar) in 10 mL H<sub>2</sub>O<sub>2</sub> (30%; Sigma-Aldrich) was prepared and then spin-coated onto the FTO-coated glass at 2000 rpm for 30 s followed by annealing in air at 500 °C for 2 h. For growth of the *nano*WO<sub>3</sub> sheets on FTO, a second precursor solution was prepared by adding 3 mL of 0.25 M H<sub>2</sub>WO<sub>4</sub> in H<sub>2</sub>O<sub>2</sub> to an aqueous HCl solution (3 mL, 1 M) containing oxalic acid (0.2 g, 99%; Sigma-Aldrich), followed by the addition of acetonitrile (10 mL, HPLC grade; Fisher Chemical) to this acidic solution. Subsequently, the precursor solution was put into a 23 mL Teflon-lined stainless steel autoclave. The FTO substrate, with a geometry area of  $4.8 \text{ cm}^2$ , modified with a WO<sub>3</sub> seed layer was vertically immersed into the second precursor solution in the autoclave, whereupon the autoclave was sealed and heated at 180 °C for 2.5 h. After the

growth of WO<sub>3</sub> nanosheets, the resulted electrode was then rinsed with ethanol, followed by annealing in air at 500 °C with a Carbolite<sup>®</sup> furnace for 1 h.

**Physical characterization of metal oxide films.** The surface morphologies of the Cu|*nano*Cu<sub>2</sub>O, the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> and the FTO|*nano*WO<sub>3</sub> electrode were characterized using a Phillips XL30-SFGE scanning electron microscope (SEM). The elemental analysis and the nanoscale images of the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> electrodes were obtained using a JEOL 3011 high resolution transmission electron microscope (HR-TEM) equipped with energy dispersive x-ray spectrometer (EDS); sample was made by scratching the film off the Cu foil and dispersing the powder in acetone under ultrasonification for 5 min. The UV-vis diffuse reflectance spectra of the Cu|*nano*Cu<sub>2</sub>O and the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> electrodes were recorded using a Cary 50 UV-vis spectrometer equipped with a diffuse reflectance accessory (Barrelino<sup>TM</sup>). The X-ray diffraction (XRD) analyses of the Cu|*nano*Cu<sub>2</sub>O, the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub>, and the FTO|*nano*WO<sub>3</sub> electrodes were carried out using an X'Pert PRO X-ray diffractometer (PANalytical B.V., The Netherland). The XPS measurements were carried out on a VG Scientific ESCALAB 250Xi electron spectrometer using a XR6 monochromated X-ray source with a 650 μm spot size. The hydrocarbon C1s line at 284.8 eV was used for energy referencing.

**Photoelectrochemical (PEC) measurement.** All electrochemical experiments were performed at 25 °C and all the potentials are reported against the normal hydrogen electrode (NHE) by using the equation  $E \text{ (V vs. NHE)} = E \text{ (V vs. Ag/AgCl)} + 0.197$ .<sup>3</sup> The measurements of the transient photocurrent density ( $J_{ph}$ ) at different potentials (E) were performed using linear sweep voltammetry at a scan rate of 10 mV s<sup>-1</sup> with an Iviumstat electrochemical working station (Ivium Technologies BV). A conventional three-electrode, one-compartment electrochemical cell was employed; the Cu|*nano*Cu<sub>2</sub>O, the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub>, or the FTO|*nano*WO<sub>3</sub> electrodes were used as the working electrode connected to a Pt foil counter electrode and a Ag/AgCl/saturated KCl reference electrode. An aqueous Na<sub>2</sub>SO<sub>4</sub> solution (0.1 M, pH 6) was used as the electrolyte in all experiments. The working electrode with exposed area of 0.2 cm<sup>2</sup> was illuminated from the front side. Electrochemical impedance spectroscopy (EIS) was performed using an electrochemical impedance analyser (CompactStat, Ivium Technologies BV, USA) with an AC amplitude of 10 mV and frequency range between 100 KHz to 0.1 Hz. All the EIS measurements were carried out with applied bias of -0.1 V under AM 1.5 light illumination (100 mW cm<sup>-2</sup>) at 25 °C. The measured EIS spectra were fitted to a suitable electrical analog by using the ZView<sup>®</sup> software (version: 3.0a; Scribner Associates Inc.)

The  $J_{ph}$ -E characteristics of a two-electrode PEC system made of the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> photocathode and the FTO|*nano*WO<sub>3</sub> photoanode were measured in a homemade two-

compartment electrochemical cell containing Na<sub>2</sub>SO<sub>4</sub> (0.1 M, pH 6). The tube-shaped anodic compartment is separated from the cathodic cell compartment by Nafion<sup>®</sup> film. The Nafion<sup>®</sup> film was filled in the tube tip by filling a Nafion<sup>®</sup> solution (0.15 mL, 5wt%, Sigma-Aldrich) and drying the Nafion<sup>®</sup> solution with a heat drier and repeating this step 5 times. Subsequently, Na<sub>2</sub>SO<sub>4</sub> (0.9 mL, 0.1 M) and a FTO|*nano*WO<sub>3</sub> electrode were introduced into the anodic compartment, and sealed with a septum. Ar gas inlet and outlet were inserted into the tube, and the removal of O<sub>2</sub> was achieved by passing a gently flow of Ar through the gas inlet for 20 min. The tightly sealed anodic compartment and the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> (N = 3) electrode were subsequently placed into the PEC cell and purged with Ar for 20 min. The I-V and η-V characteristics for the two-electrode system were measured under standardized solar light illumination. Both electrodes had an exposed geometric surface area of 0.5 cm<sup>2</sup>.

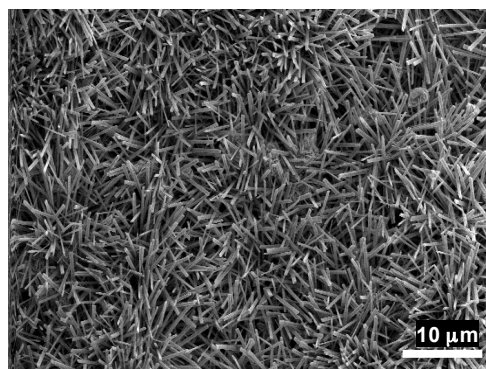
**Hydrogen measurement.** The amount of H<sub>2</sub> generated was detected and quantified by headspace gas analysis with an Agilent 7890A Series GC equipped with a 5 Å molecular sieve column (N<sub>2</sub> carrier gas at a flow rate of approximately 3 mL min<sup>-1</sup>). The GC oven holding the columns was kept at 40 °C, and a thermal conductivity detector was used. The electrochemical cell was purged with 2% CH<sub>4</sub> in N<sub>2</sub> for at least 20 min prior PEC experiments; methane acts as an internal standard for H<sub>2</sub> quantification by gas chromatography (GC). A 50 μL aliquots of the headspace gas was removed from the air-tight electrochemical cell for GC analysis after applying the charge of 0.33 C (at -0.36 V vs. NHE for three-electrode system) or 0.12 C (at -0.6 V for two-electrode system).

**Oxygen measurement.** Oxygen was detected quantitatively in headspace of the anodic compartment of the PEC cell by using an Ocean Optics fluorescence oxygen probe (FOXY-R). The probe was inserted through a tightly sealed septum and continuous O<sub>2</sub> readings (O<sub>2</sub> partial pressure) at 1 s intervals were made throughout the experiment (Fig. S7). The cell was operated at applied voltage of -0.6 V in dark in first 30 min (control experiment), followed by 30 min water splitting under standardized light illumination (100 mW cm<sup>-2</sup>) at applied voltage of -0.6 V, and another 30 min in dark at applied voltage of -0.6 V in dark (control experiment). The total amount of O<sub>2</sub> evolved was calculated from the amount of O<sub>2</sub> measured in the headspace using the ideal gas law.

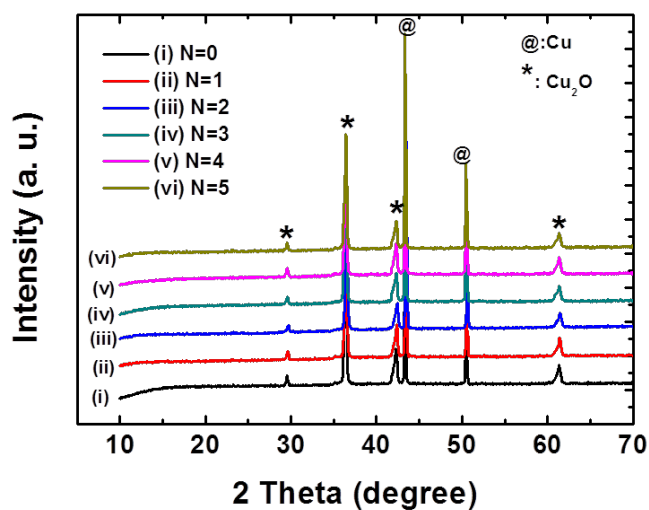
**Light sources.** Visible light irradiation was provided either by an LED white light (425 to 660 nm) source (ModuLight, Ivium Technologies BV, USA) or a solar light simulator equipped with an air mass 1.5 global filter and an IR water filter (Newport Oriel, 150 W). The intensity of LED light irradiation was 26 mW cm<sup>-2</sup> (measured using a Newport High Power Detector equipped with a Newport 1916-R Handheld Optical Power Meter). The light intensity of the solar light simulator was 100 mW cm<sup>-2</sup> (1 sun) and this light source was designated as the standardized solar light.

## References.

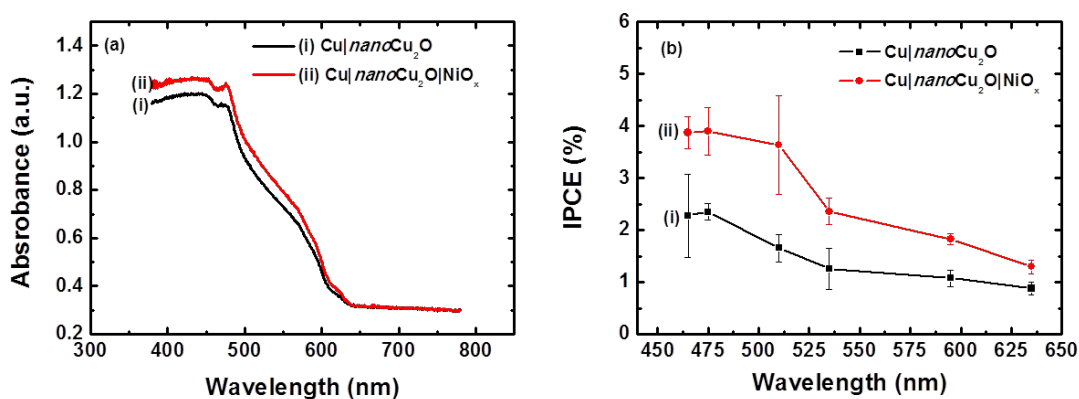
1. W. X. Zhang, X. G. Wen, S. H. Yang, Y. Berta and Z. L. Wang, *Adv. Mater.*, 2003, **15**, 822-825.
2. J. Z. Su, X. J. Feng, J. D. Sloppy, L. J. Guo and C. A. Grimes, *Nano Lett.*, 2011, **11**, 203-208.
3. D. J. G. Ives and G. J. Janz, *Reference electrodes, theory and practice.*, Academic Press, New York, 1961.



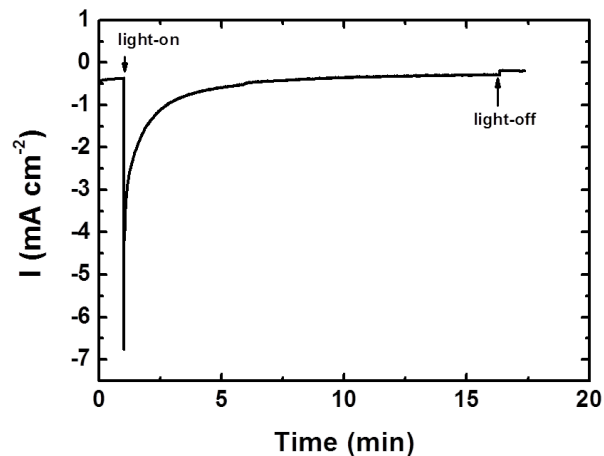
**Figure S1.** SEM image of the Cu|*nano*Cu(OH)<sub>2</sub> with magnification of 2,000X.



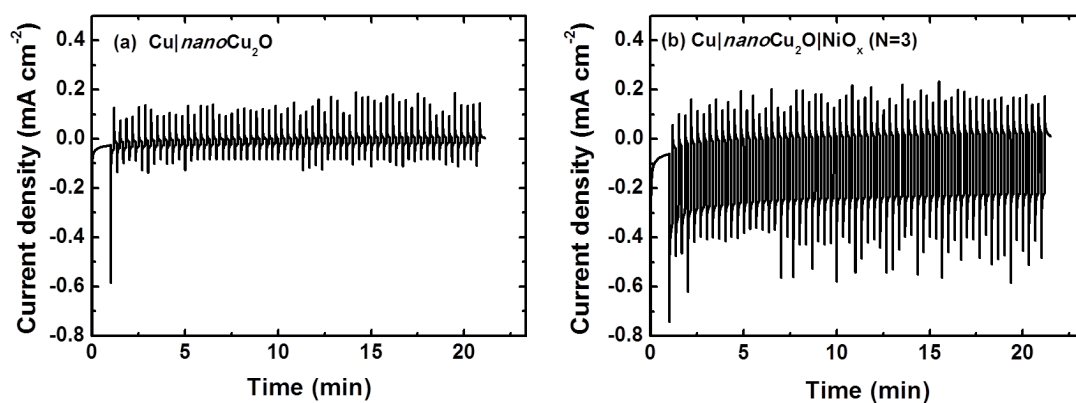
**Figure S2.** XRD patterns of the Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> electrodes with various layer numbers (N) of NiO<sub>x</sub>. XRD of the Cu|*nano*Cu<sub>2</sub>O is shown as N = 0.



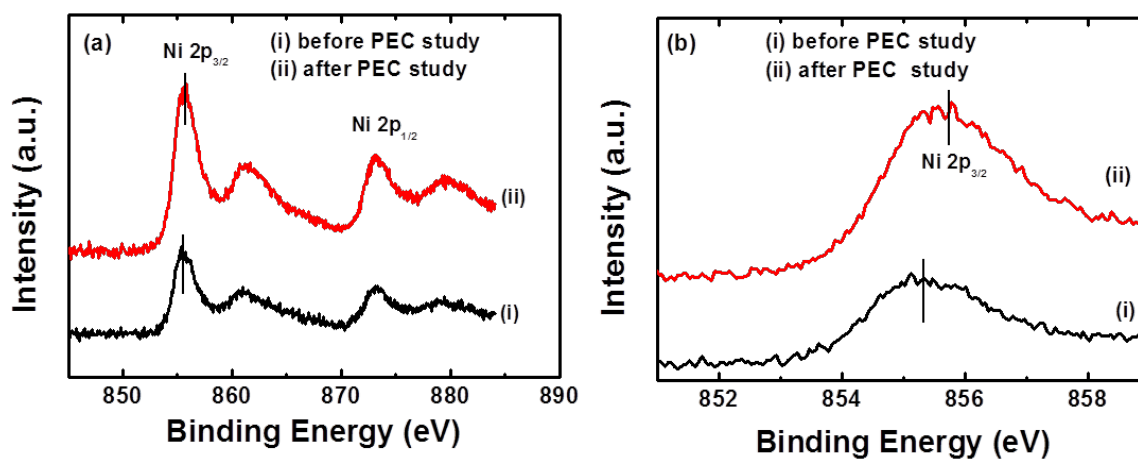
**Figure S3.** (a) Diffuse reflectance UV-vis spectra and (b) photocurrent spectra for the Cu|nanoCu<sub>2</sub>O and the Cu|nanoCu<sub>2</sub>O|NiO<sub>x</sub> (N=3). Photocurrent spectra were measured at applied potential of 0.1 V vs. NHE in an aqueous Na<sub>2</sub>SO<sub>4</sub> electrolyte under LED light illumination at various wavelengths. Monochromatic incident photon-to-electron conversion efficiency (IPCE) was calculated using formula:  $J_{ph} \times 1240 / \lambda \times P_{in}$ ,  $J_{ph}$  is photocurrent density ( $\text{mA cm}^{-2}$ ),  $\lambda$  is wavelength (nm), and  $P_{in}$  is the incident light intensity ( $\text{mW cm}^{-2}$ ).



**Figure S4.** Transient current density (I) of the unmodified Cu|nanoCu<sub>2</sub>O electrode at -0.36 V vs. NHE under continuous standardized solar light illumination with Ar purging.

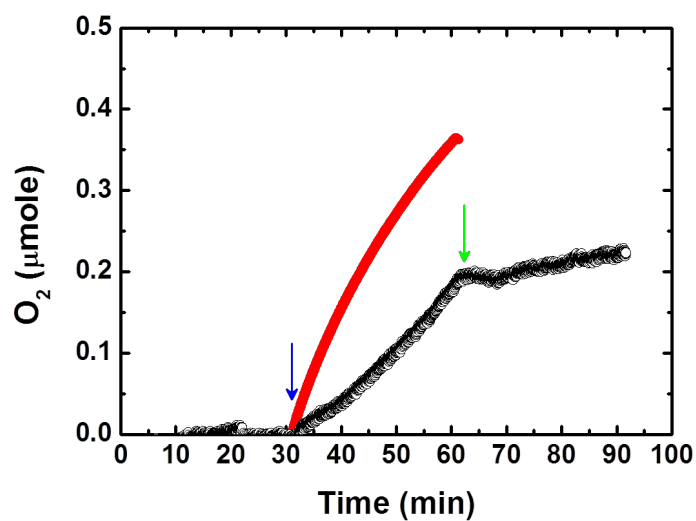


**Figure S5.** Transient photocurrent density responses of (a) the Cu|nanoCu<sub>2</sub>O and (b) the Cu|nanoCu<sub>2</sub>O|NiO<sub>x</sub> (N = 3) electrodes at 0.1 V vs. NHE under chopped AM 1.5 light illumination ( $\sim 100 \text{ mW cm}^{-2}$ ) with Ar purging.



**Figure S6.** (a) The XPS spectra of Ni 2p of the Cu|nanoCu<sub>2</sub>O|NiO<sub>x</sub> (N = 3) (i) before and (ii) after PEC experiment, which was carried out at 0.1 V vs. NHE under chopped LED light illumination ( $\sim 26 \text{ mW cm}^{-2}$ ). (b) Enlarged part of (a).





**Figure S7.** O<sub>2</sub> evolution during PEC water splitting with a two-electrode cell using a Cu|*nano*Cu<sub>2</sub>O|NiO<sub>x</sub> (N = 3) photocathode and a FTO|*nano*WO<sub>3</sub> photoanode. A bias of -0.6 V was applied throughout the whole experiment, but standardized solar light only applied between 30 and 60 min (blue and green arrows indicate the beginning and the end of PEC water splitting, respectively). The amount of O<sub>2</sub> was quantified by an O<sub>2</sub> fluorescence probe (black trace) and the theoretical amount of O<sub>2</sub> with 100 % Faradaic efficiency is shown as a red trace.