

## Engineering Cu<sub>2</sub>O/NiO/Cu<sub>2</sub>MoS<sub>4</sub> Hybrid Photocathode for H<sub>2</sub> Generation in Water

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### Supporting Information

**General:** Chemical compounds were used as received from Sigma Aldrich without further purification. Fluorine-doped tin oxide (FTO, 400 nm) coated on glass substrate (2.2 mm) having sheet resistance of 14 Ohm/sq was purchased from NSG group. FTO electrodes were intensively cleaned by subsequent ultrasonication in acetone, ethanol and DI water and kept in DI water. Prior to used, these FTO electrodes were dried with a N<sub>2</sub> flux. Cu<sub>2</sub>MoS<sub>4</sub> nanopowders were prepared as described previously.<sup>1</sup>

**Cu<sub>2</sub>O thin film deposition.** Cu<sub>2</sub>O thin films were electrodeposited on FTO electrode from a 0.4 M CuSO<sub>4</sub> bath containing 3 M lactic acid, employing a conventional three electrodes configuration. pH of the deposition bath was carefully adjusted to pH 12.0 by adding 4 M NaOH. FTO electrode was hold at constant cathodic potential of -0.4V vs Ag/AgCl reference. Film thickness was controlled by counting charge passing through the working electrode. The deposition was ended when the charge density value reached 2C.cm<sup>-2</sup>.

**NiO layer deposition.** 50 μL of a 0.5M nickel (II) acetate (Ni(OAc)<sub>2</sub>) solution in 2-methoxyethanol containing 0.5 M ethanolamine was spin-coated on the Cu<sub>2</sub>O electrode (geometrical surface area of 2.25 cm<sup>2</sup>) with 3000 rpm for 30 s, followed by annealing in air at 220 °C for 30 min. The thickness of the NiO layer on the Cu<sub>2</sub>O electrode was controlled by repeating this process N (N=1-5) times.

**Coating Cu<sub>2</sub>MoS<sub>4</sub> electrocatalyst layer.** A stock suspension was prepared by dispersing 8 mg Cu<sub>2</sub>MoS<sub>4</sub> nanopowders in 2 mL H<sub>2</sub>O/ Ethanol (v/v =4/1) mixture with aid of ultrasonication for 2 hours. 50 μL of the stock suspension was drop-casted on 2.25 cm<sup>2</sup> Cu<sub>2</sub>O/NiO electrode surface. Obtained hybrid electrodes Cu<sub>2</sub>O/NiO/Cu<sub>2</sub>MoS<sub>4</sub> were air-dried prior used for characterization.

### **Characterization**

Field Emission Scanning Electron Microscopic (FESEM) was carried out using a JEOL JSM-7600F scanning electron microscope to obtain surface morphology information as well as the film thickness. The phase and crystallinity were investigated by X-ray diffractometer (XRD, X<sup>3</sup>pert Pro MRD, Philips, using Cu K $\alpha$  radiation  $\lambda = 1.54\text{\AA}$ ).

The chemical composition and the valance band-to-Fermi level difference were investigated by X-ray Photoelectron Spectroscopy (XPS) using an ultrahigh vacuum VG ESCALAB 220i-XL system equipped with a monochromatic Al K $\alpha$  (1486.6eV) source. The pressure in the analysis chamber was kept in the 10<sup>-10</sup> Torr range. The hemispherical energy analyzer was calibrated with gold, silver and copper polycrystalline standard samples by setting the Au4f<sub>7/2</sub>, Ag3d<sub>5/2</sub> and Cu2p<sub>3/2</sub> peaks at binding energies of 83.98±0.02, 368.26±0.02 and 932.67±0.02 eV.

### **Assay photoelectrochemical properties of Cu<sub>2</sub>O-based photocathodes**

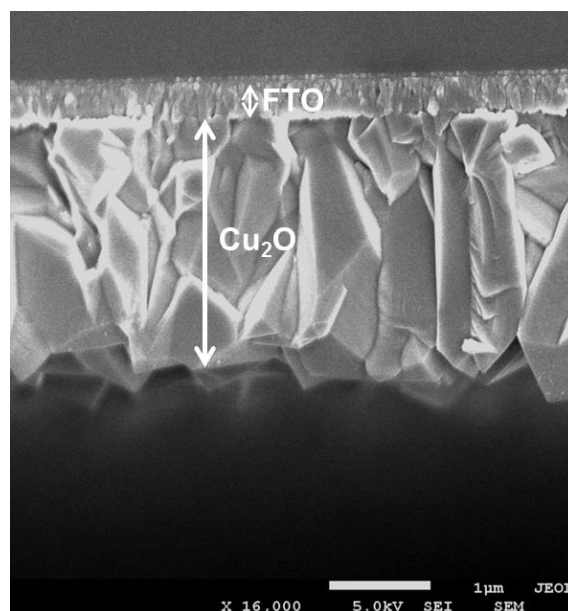
The photoelectrochemical measurement was conducted on a potential station (CHI 660D work station) with employing a conventional three electrodes configuration. Platinum wire and Ag/AgCl/ 3M KCl were employed as counter and reference electrodes, respectively. Cu<sub>2</sub>O working electrode (photoactive area of ~ 0.23cm<sup>2</sup>) was illuminated from back-side (glass side) by 1 Sun light generated from a simulated AM 1.5 light source. The electrolyte was a 1.0M Na<sub>2</sub>SO<sub>4</sub> solution buffered by 1M NaHSO<sub>4</sub> to pH 5. Prior to measurement, the electrolyte solution was intensively saturated with N<sub>2</sub> gas to remove solubilized O<sub>2</sub>. Potential scan rate for the linear sweep voltammetry and for the cyclic voltammetry analysis was 20mV.s<sup>-1</sup>. Photocurrent stability tests were carried out by measuring the photocurrent produced under chopped light irradiation (light/dark cycles of 20 s) at a fixed electrode potential.

All potentials are quoted versus the *Reversible Hydrogen Electrode* (RHE) by using the following equation:

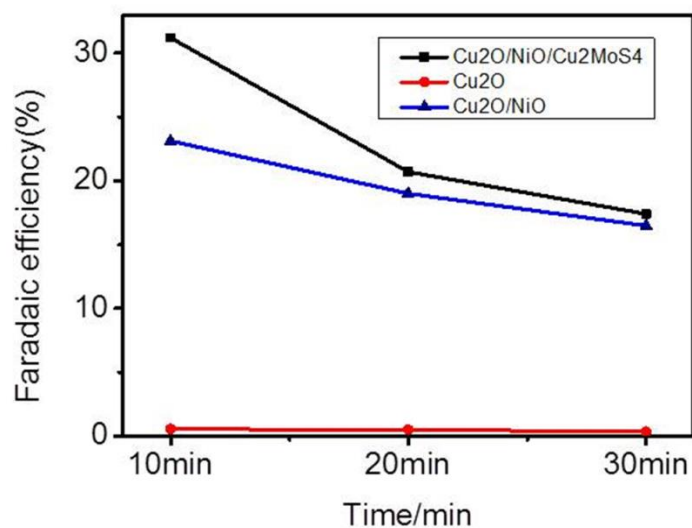
$$E_{vs. RHE} = E_{vs. Ag/AgCl} + 0.059pH + 0.21V$$

To quantify produced  $H_2$ , a gas-tight closed electrochemical cell was employed. The counter electrode and reference electrode were Pt wire and Ag/AgCl/ 3M KCl, respectively.  $Cu_2O$ -based photocathode having photoactive surface area of  $1.5cm^2$  was hold at a fixed potential (+0.3V *vs.* RHE) and under 1 Sun illumination for a period of 30 min. Once the bulk photo-electrolysis was over, photo-generated  $H_2$  gas was quantified using a gas chromatography equipped thermal couple detector (TDC).

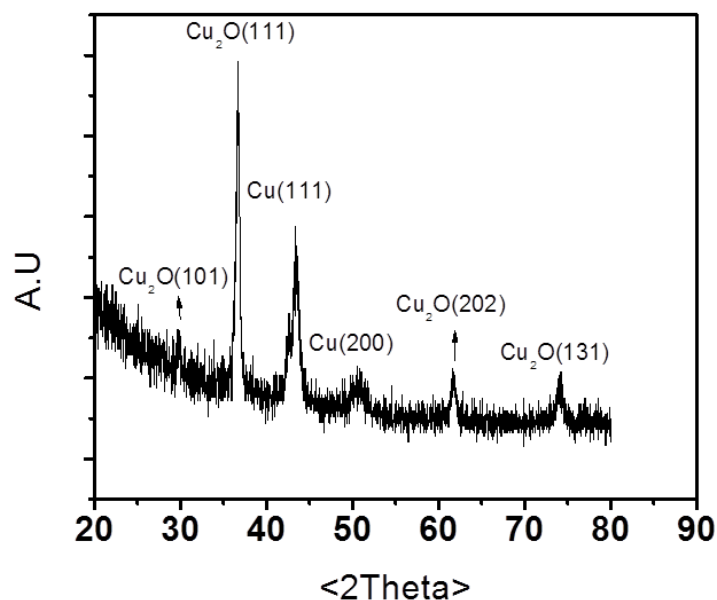
Electrochemical impedance spectroscopy (EIS) analysis was conducted for  $Cu_2O$ -based photoelectrodes employing the same three-electrode configuration stated this above. The measurements were performed with a potentiostat Autolab PGSTAT-30 equipped with a frequency analyser module. The  $Cu_2O$ -based photocathodes were hold at +0.3V *vs.* RHE under 1 Sun illumination. A small voltage perturbation (20 mV rms) was applied with frequencies ranging between 100 kHz and 0.1 Hz. The results were fitted to the equivalent circuit presented in **figure S10** with a ZView software by Scribner Associated.



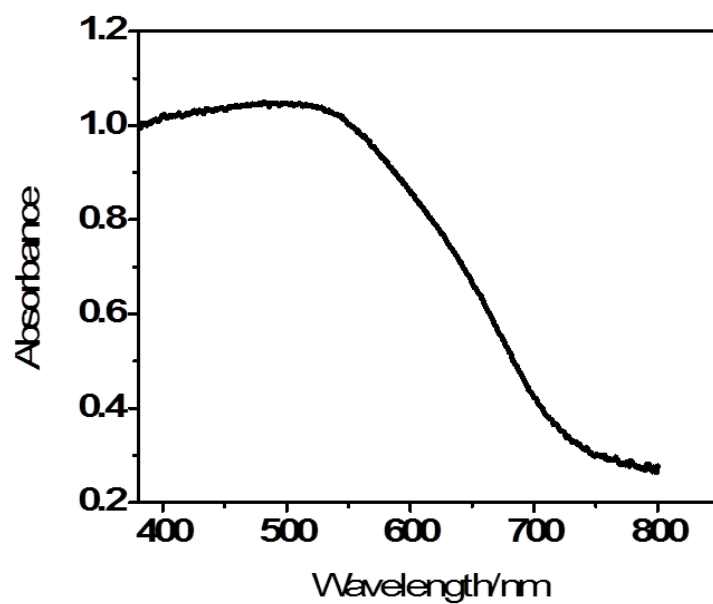
**Figure S1:** SEM cross-section analysis for a  $Cu_2O$  thin film electrodeposited on a FTO electrode



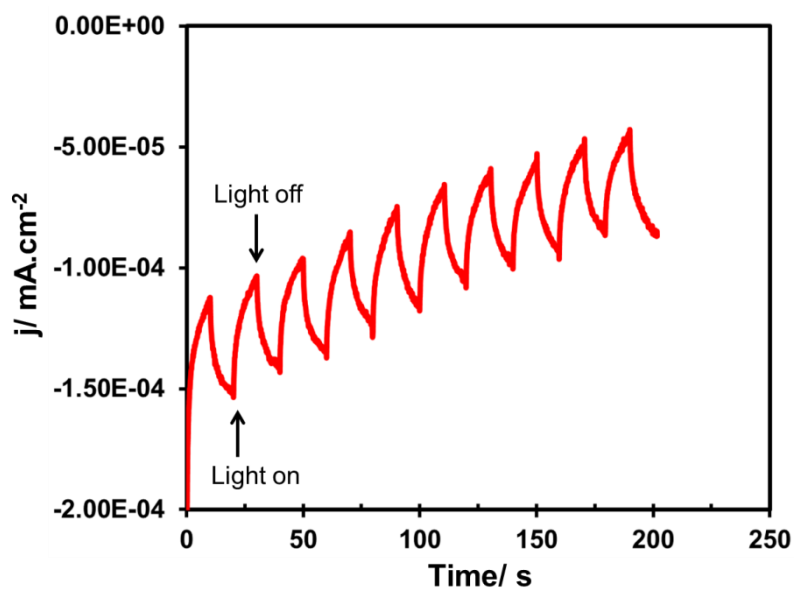
**Figure S2:** Photocurrent-to- $H_2$  yield (Faradaic efficiency) calculated on the basis of bulk photoelectrolysis experiments at +0.3V vs. RHE employing a  $Cu_2O$  (red curve) or a  $Cu_2O/NiO/Cu_2MoS_4$  (black curve), or at 0V vs. RHE employing a  $Cu_2O/NiO$  (blue curve) photocathode without  $Cu_2MoS_4$  co-catalyst.



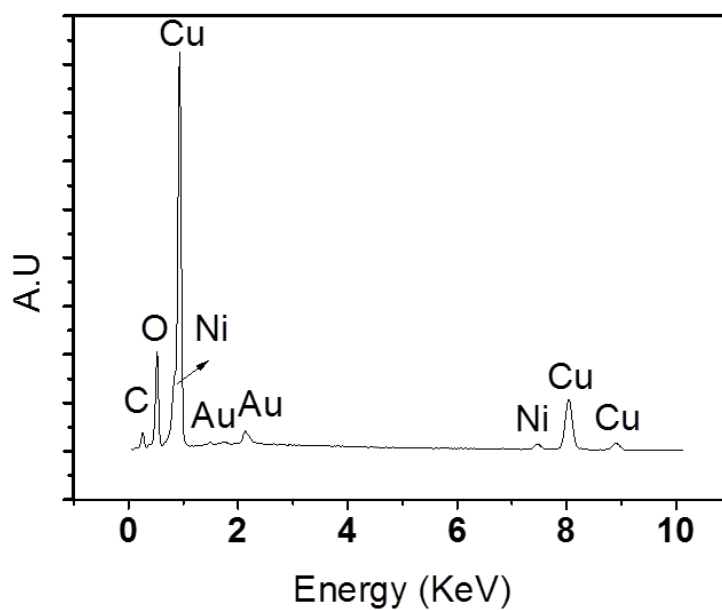
**Figure S3:** XRD pattern of a  $Cu_2O$  photoelectrode after 30min photoelectrolysis in pH 5  $Na_2SO_4$  solution, under 1 Sun illumination at +0.3V vs. RHE



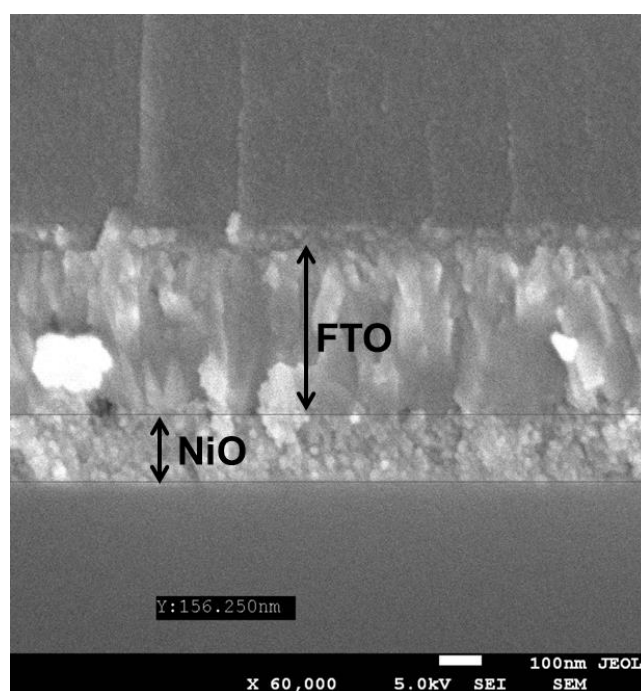
**Figure S4:** Diffuse reflectance UV-vis absorption spectrum of  $\text{Cu}_2\text{MoS}_4$



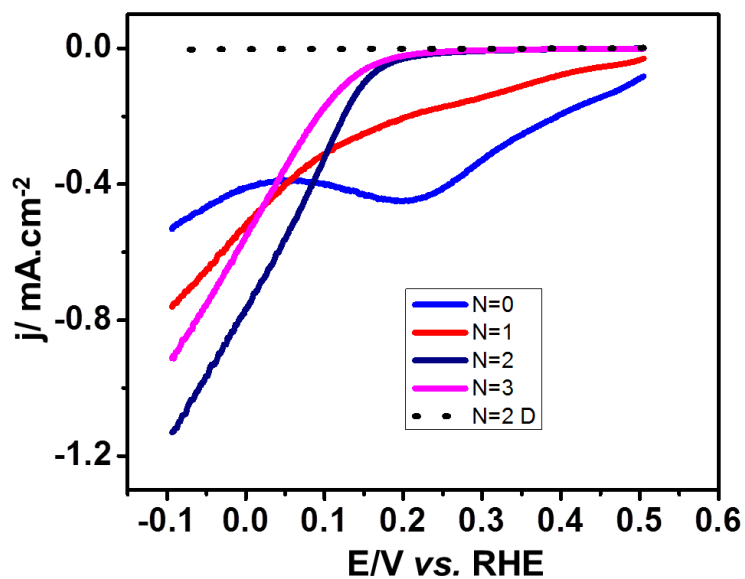
**Figure S5:** Anodic photocurrent collected on a  $\text{NiO}/\text{Cu}_2\text{MoS}_4$  electrode under 1 Sun chopped light illumination at applied potential of  $+0.3\text{V}$  vs. RHE. Electrolyte was a pH 5  $\text{Na}_2\text{SO}_4$  solution.



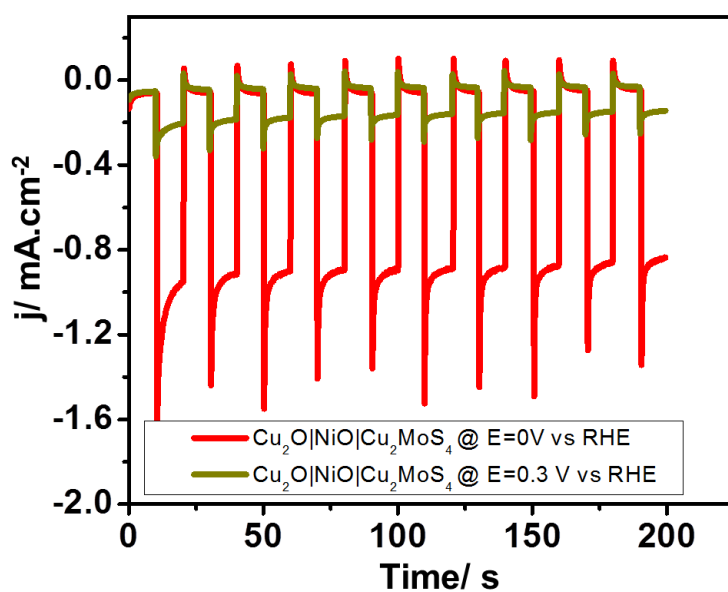
**Figure S6:** EDX analysis performed on an as-prepared  $\text{Cu}_2\text{O}/\text{NiO}$  electrode. Au signal comes from sputtered conductive Au films



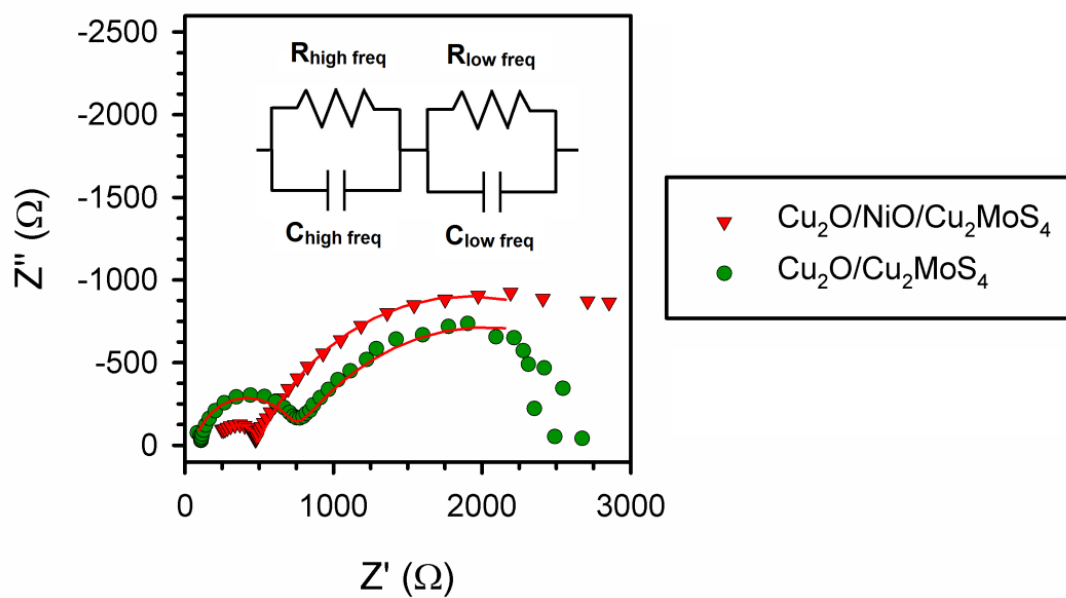
**Figure S7:** SEM analysis cross-section view for a NiO film deposited on FTO substrate by repeating 10 deposition cycles ( $N=10$ ).



**Figure S8:** Photoelectrochemical properties of  $\text{Cu}_2\text{O}/\text{NiO}$  photoelectrodes with varied NiO thickness.  $N$  represents number of NiO deposition cycles. Average NiO thickness was estimated to be 16nm per deposition cycle.

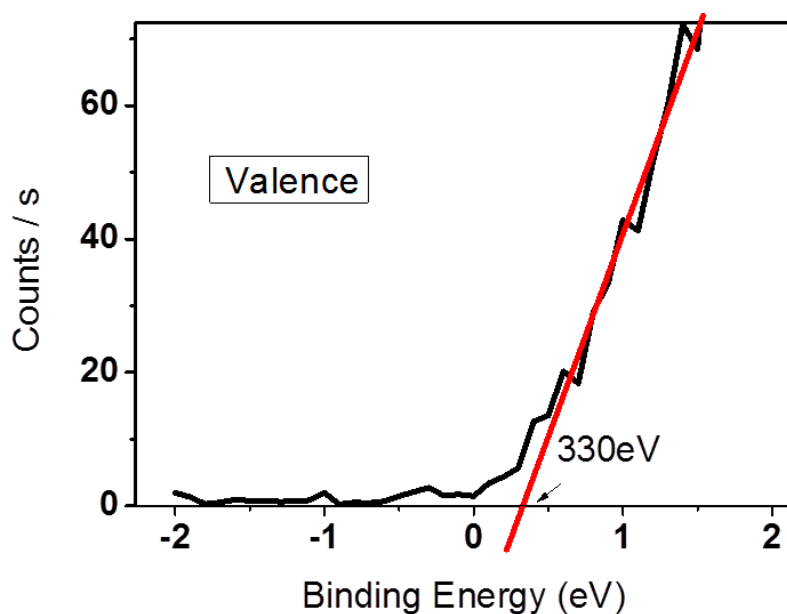


**Figure S9:** Photocurrent generated employing a  $\text{Cu}_2\text{O}/\text{NiO}/\text{Cu}_2\text{MoS}_4$  hybrid photocathode under 1 Sun illumination in pH 5  $\text{Na}_2\text{SO}_4$  electrolyte solution at applied bias of 0 and +0.3V vs. RHE.



**Figure S10:** Nyquist plots analysis performed on  $\text{Cu}_2\text{O}/\text{Cu}_2\text{MoS}_4$  hybrid photocathode with and without a NiO interlayer. The solid lines represent the fittings using the model in the inset. Electrolyte was a pH 5  $\text{Na}_2\text{SO}_4$  buffered solution. Electrodes were hold at +0.3V vs. RHE under 1 Sun illumination.





**Figure S11:** High-resolution valence-band XPS spectra shows the difference of the Fermi level and valance band of NiO is only around 300 mV.

**Table S1:** Parameters extracted from the fitting of the data in figure S10.

Cell	$R_{\text{high freq}}$ ( $\pm 15 \Omega$ )	$C_{\text{high freq}}$ ( $\pm 0.5 \cdot 10^{-8} \text{ F}$ )	$R_{\text{low freq}}$ ( $\pm 160 \Omega$ )	$C_{\text{low freq}}$ ( $\pm 0.5 \cdot 10^{-5} \text{ F}$ )
$\text{Cu}_2\text{O}/\text{Cu}_2\text{MoS}_4$	651	$4.1 \cdot 10^{-8}$	2620	$3.6 \cdot 10^{-5}$
$\text{Cu}_2\text{O}/\text{NiO}/\text{Cu}_2\text{MoS}_4$	211	$1.6 \cdot 10^{-8}$	2780	$4.7 \cdot 10^{-5}$

## References

- 1 Tran, P. D. *et al.* Copper molybdenum sulfide: a new efficient electrocatalyst for hydrogen production from water. *Energy & Environmental Science* **5**, 8912, doi:10.1039/c2ee22611a (2012).