Electronic Supplementary Information (ESI)

Copper Nickel Mixed Oxide Hole Selective Layer for Au-Free Transparent Cuprous Oxide Photocathodes

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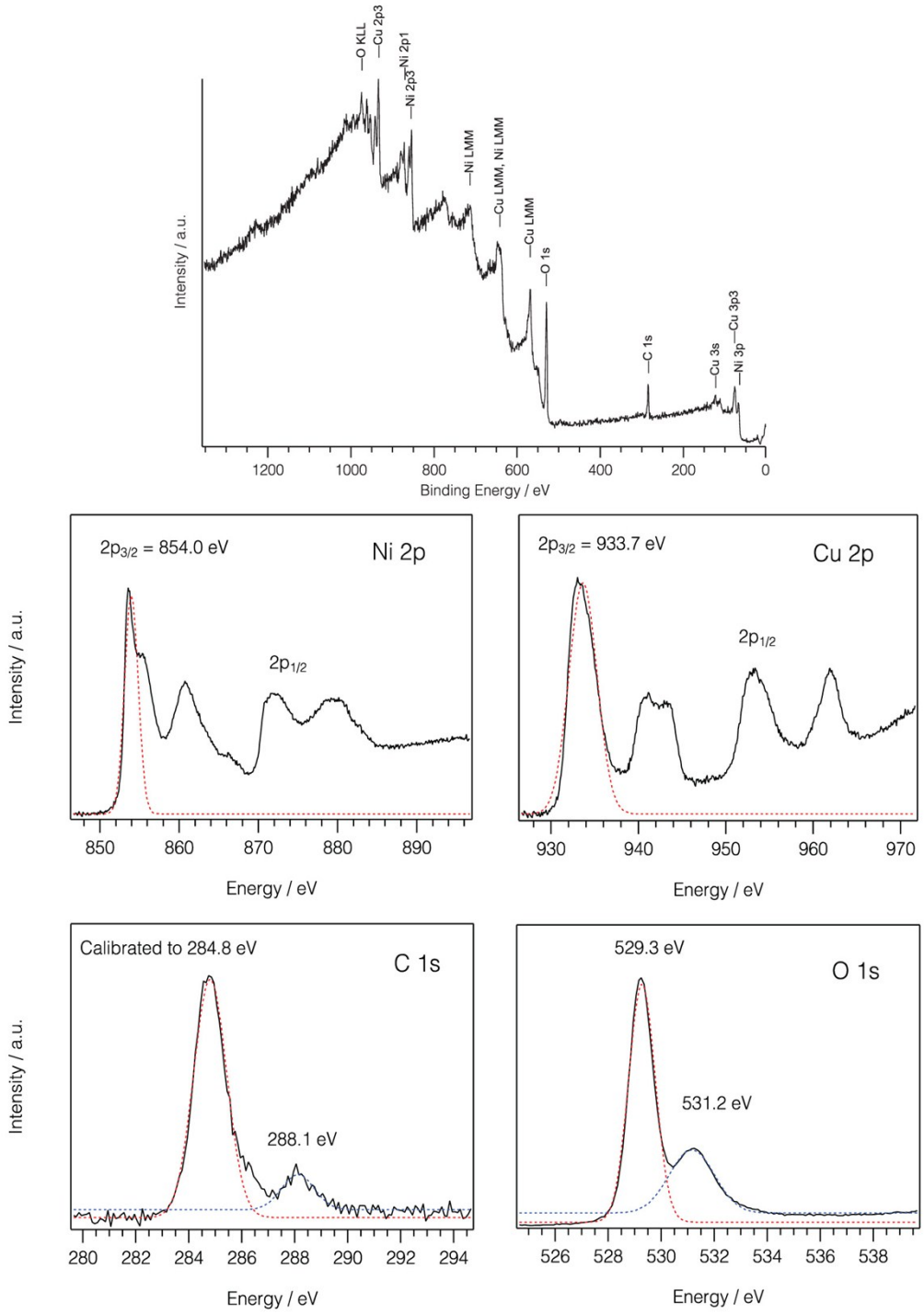

Figure S1. XPS spectra of 4.4 nm CuO/NiO film deposited on FTO. XPS measurement was carried out at the sample surface without further cleaning.

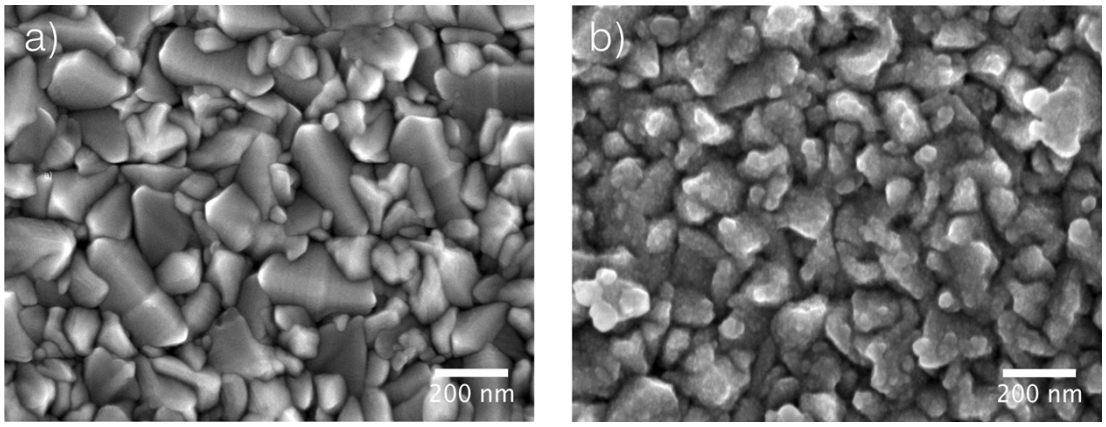

Figure S2. Top-view SEM image of Ni (2 nm)/Cu (0.4 nm)/Ni (2nm) film deposited on FTO a) before and b) after annealing at 450 ^{o}C for 20 min in air.

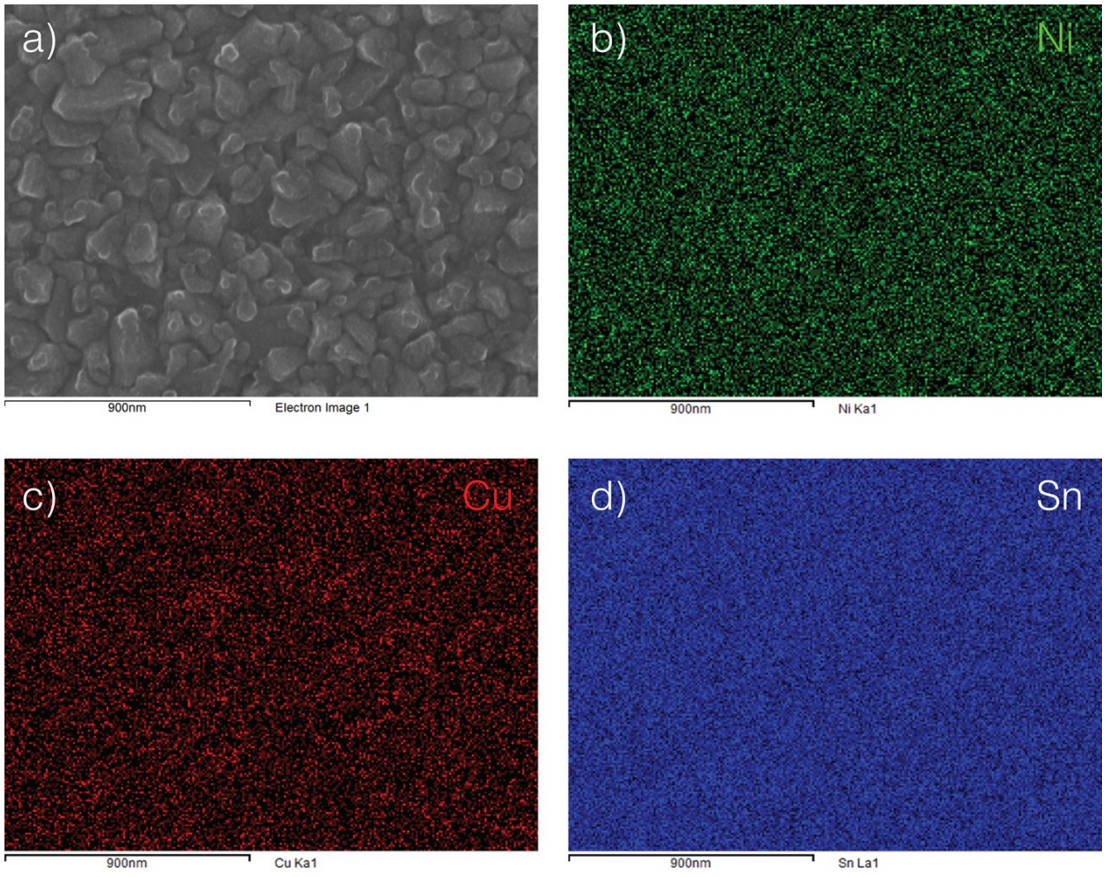

Figure S3. Top-view SEM image and EDX characterization of 4.4 nm CuO/NiO film deposited on FTO. a) Top-view SEM image and element mapping of b) Ni, c) Cu and d) Sn, respectively.

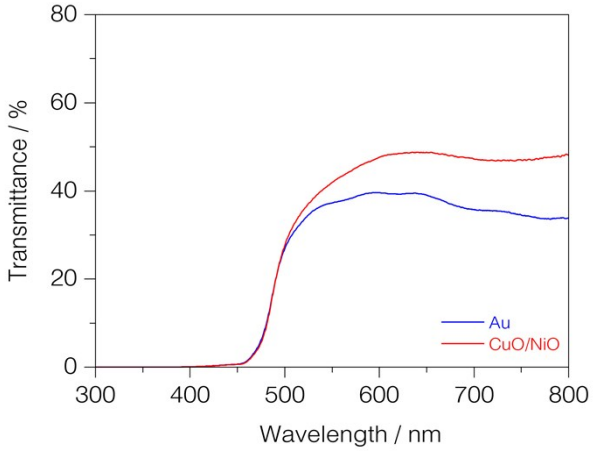

Figure S4. Transmittance spectra of $RuO_x/TiO_2/AZO/Cu_2O$ photocathode with a Cu_2O thickness 200 nm on 3 nm thick Au (blue) and 4.4 nm thick CuO/NiO (red) deposited FTO.

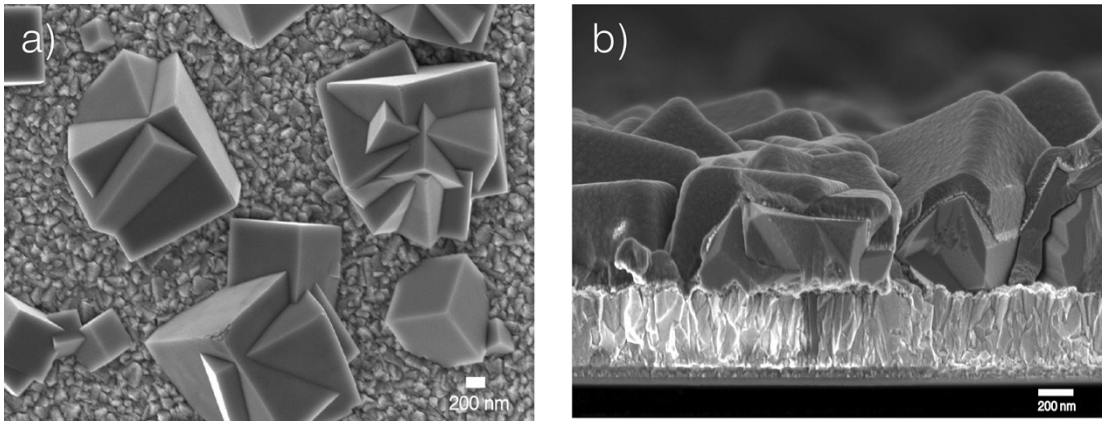

Figure S5. a) Top-view SEM image of Cu_2O electrode on 4 nm thick NiO film after electrodepositing Cu_2O for 30 min. b) Cross-section SEM image of Cu_2O photocathode on 4 nm thick NiO film with Cu_2O electrodeposition for 50 min, AZO/TiO_2 overlayers and RuO_x HER catalyst.

Optimization of CuO/NiO layer and Cu_2O thickness

The annealing temperature for oxidizing the sputtered metal film is important because it can have an influence on the electrical characteristics of the CuO/NiO film. The Cu_2O thickness is a significant parameter affecting the performance and transparency of the Cu_2O photocathode. Therefore, the annealing temperature and Cu_2O deposition time were controlled to optimize the Cu_2O photocathode on the CuO/NiO film. First, the fill factor of the photocurrent–voltage curves improved at annealing temperatures above 350 °C reaching its optimum at 450 °C (Figure S6a). This has been attributed to a decrease in resistivity of the Cu-Ni mixed oxide film.[1] Second, the best performance was shown when the Cu_2O deposition time was set to 30 min, corresponding to a Cu_2O thickness of 200 nm (Figure S6b). The plateau current density was slightly improved with increasing Cu_2O thickness, while the photocurrent onset became resistive when the Cu_2O thickness was above 200 nm. The

enhanced light utilization in the longer wavelength region led to an improved photocurrent density at 0 V versus RHE according to the increased Cu_2O thickness (Figure S6c). However, the relative difference in photocurrent densities (at 0 V versus RHE) for frontside and backside illumination ($\Delta J = (J_{front} - J_{back})/J_{front}$) was increased along with the increase of Cu_2O thickness (Figure S6d). This means that the electron transport is severely impeded in the thicker Cu_2O film, which is supported by the IPCE spectra shown in Figure S6c. A considerable loss of IPCE in the short wavelength region below 470 nm is seen for backside illumination. Especially, the ΔJ reached up to around 30% when the Cu_2O thickness was 320 nm. Consequently, 450 °C and 30 min were selected as the optimal annealing temperature and Cu_2O electrodeposition time in this work.

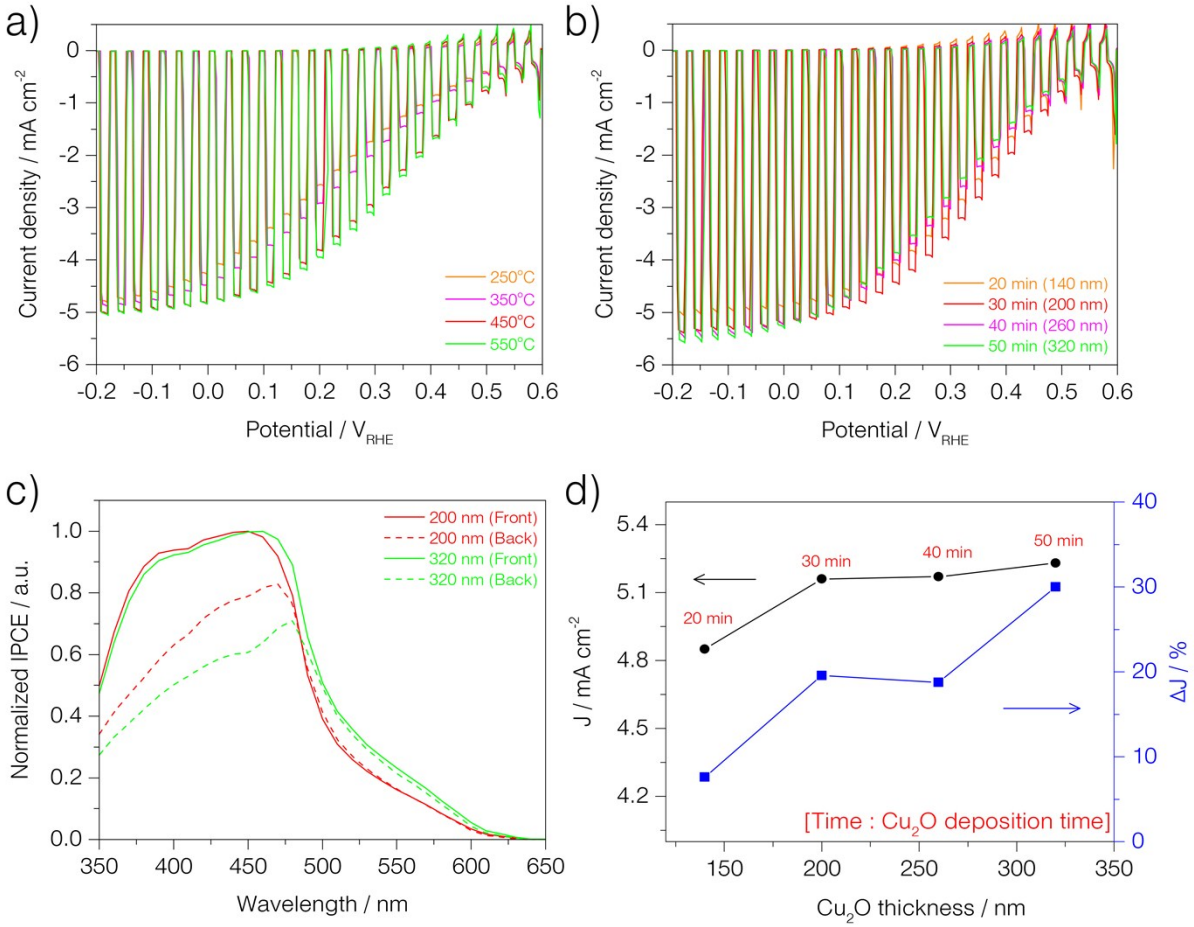

Figure S6. J-V characteristics of Cu_2O photocathode with a) Cu_2O electrodeposition for 25 min on 4.4 nm thick CuO/NiO annealed at different temperatures for 20 min in air and b) different Cu_2O electrodeposition time (Cu_2O thickness) on 4.4 nm thick CuO/NiO annealed at 450 °C for 20 min in air under chopped illumination in pH 5 electrolyte to optimize the conditions for the CuO/NiO based Cu_2O photocathode. c) Normalized IPCE spectra of Cu_2O photocathode with thicknesses of 200 nm and 320 nm under frontside and backside illumination, which were normalized at their peak values. d) Absolute photocurrent density (J) and relative difference in photocurrent densities for frontside and backside illumination [$\Delta J = (J_{front} - J_{back})/J_{front}$] of Cu_2O photocathode with different thicknesses. The 4.4 nm thick CuO/NiO film was prepared by annealing at 450 °C for 20 min in air and measurements were carried out under an applied potential of 0 V versus RHE in pH 5 electrolyte in c) and d).

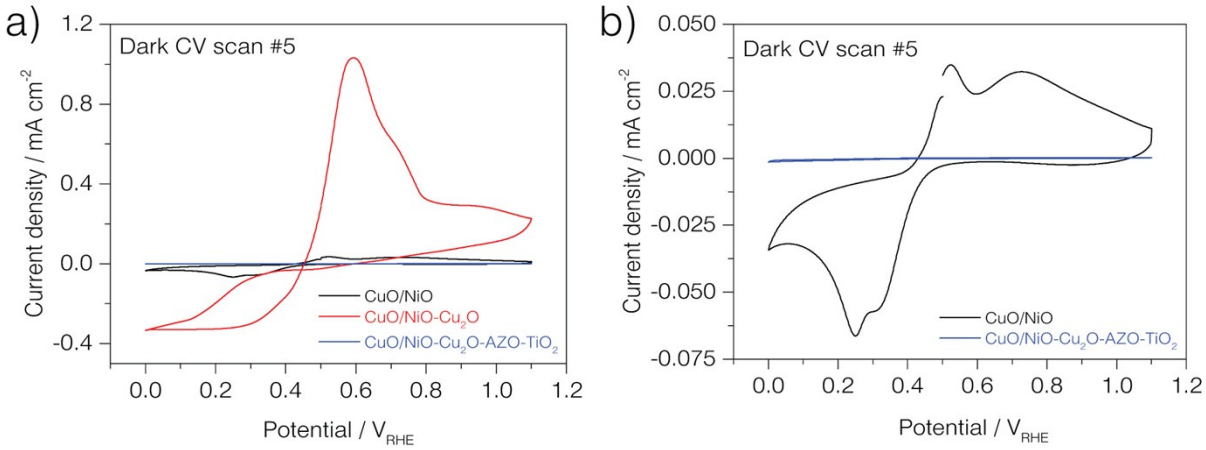

Figure S7. a) Cyclic voltammetry (CV) of CuO/NiO (black), Cu_2O deposited on CuO/NiO (CuO/NiO-Cu_2O, red) and TiO_2-AZO overlayered Cu_2O on CuO/NiO (CuO/NiO-Cu_2O-AZO-TiO_2, blue) and b) magnified-scale CV of CuO/NiO and CuO/NiO-Cu_2O-AZO-TiO_2 in the dark in pH 5 electrolyte. The scan rate was 10 mV s^{-1}. While CuO/NiO and Cu_2O are susceptible to electrochemical corrosion in contact with water, the AZO-TiO_2 protected Cu_2O photocathode shows no reduction or oxidation peaks.

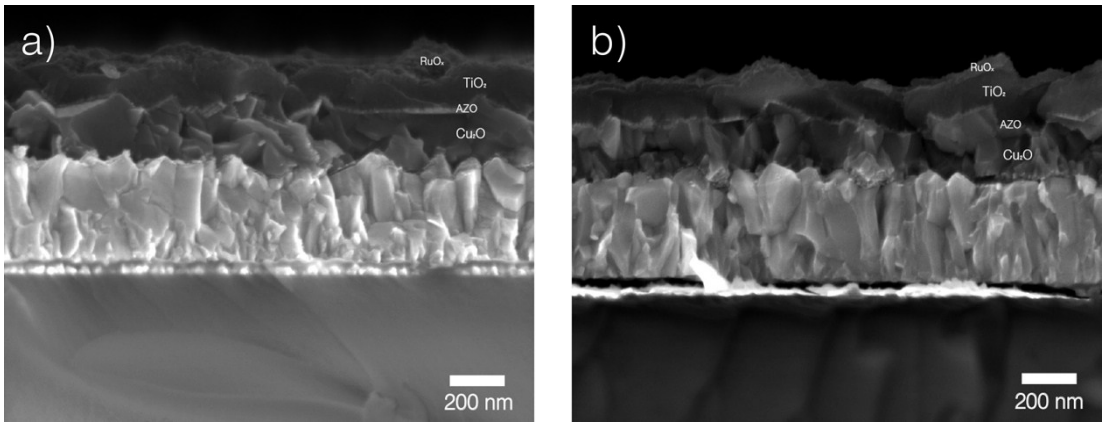

Figure S8. Cross-section SEM image of Cu_2O photocathode on a) 4.4 nm thick CuO/NiO coated FTO and b) 3 nm thick Au coated FTO with AZO/TiO_2 overlayers and RuO_x HER catalyst. The Cu_2O electrodeposition time was 30 min.

Mott-Schottky analysis

Impedance data were fitted in ZView to a Randles circuit to extract the capacitance. Mott-Schottky plots showed p-type characteristics of our CuO/NiO and Cu_2O films (Figure S9). Flatband potential and charge carrier densities were extracted using the Mott-Schottky equation for p-type semiconductors:

$$\left(\frac{A}{C_{bulk}}\right)^2 = \frac{2}{e\varepsilon_r\varepsilon_0 N_A}\left(V - V_{fb} + \frac{kT}{e}\right)$$

where e is the electronic charge, ε_r is the relative permittivity of materials, ε_0 is the

permittivity of vacuum, N_A is the carrier concentration, k is the Boltzman constant, T is the absolute temperature, A is the area of electrode, V is the applied potential and V_{fb} is the flat band potential.[2] V_{fb} of CuO/NiO and Cu_2O deposited on CuO/NiO were determined through a linear fit in the linear region of the Mott-Schottky plot and were calculated to be 0.57 V and 0.62 V versus RHE, respectively.

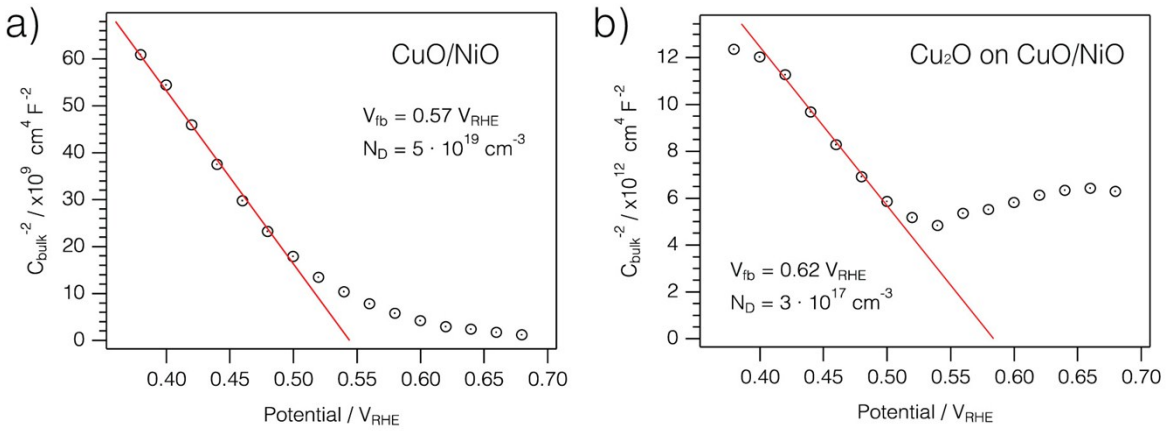

Figure S9. Mott-Schottky plots of a) 20 nm CuO/NiO film on FTO and b) 200 nm Cu_2O film on 4.4 nm thick CuO/NiO film obtained from impedance measurement in the dark in pH 7.67.

Diffuse reflectance measurement of CuO/NiO

Figure S10 shows a graphical representation derived from the diffuse reflectance of a 9.2 nm thick CuO/NiO film on quartz using Kubelka-Munk theory.[3] The energy extracted from the blue line is similar to the NiO band gap energy, while the tail of red curve is reached to near CuO band gap energy. This well supports that our CuO/NiO film is a mixture of NiO and CuO. To estimate band gap of CuO/NiO film for constructing a relative band alignment, we chose the energy extracted from blue line because NiO is more dominant than CuO in the CuO/NiO film.

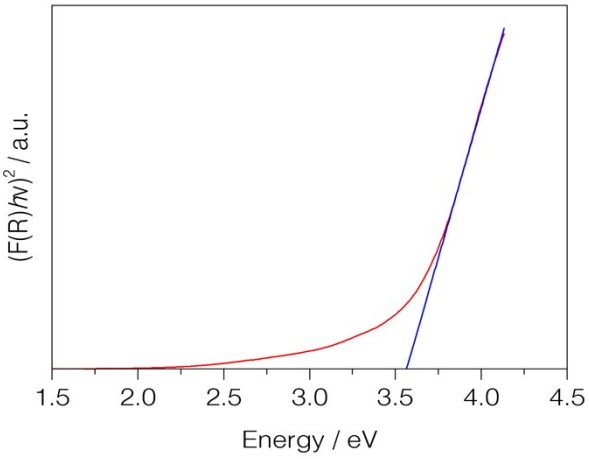

Figure S10. Graphical representation of modified Kubelka-Munk derived from the diffuse reflectance of a 9.2 nm thick CuO/NiO film on quartz. The CuO/NiO film was fabricated by sequential sputtering 2 nm Ni/3x(0.4 nm Cu/2 nm Ni) and annealing at 450 °C for 20 min in air.

Table S1. Electrical properties obtained from hall measurement of 40 nm CuO/NiO film and 100 nm NiO on the non-conductive glasses.

	CuO/NiO	NiO
Carrier Density, N_A / cm^{-3}	4.3 x 10^{16}	3.1 x 10^{15}
Mobility, μ / $cm^2 V^{-1} s^{-1}$	3.1	4.0
Resistivity, ρ / Ω cm	48	512

Notes and references

1. Y.A.K. Reddy, A.S. Reddy, P.S. Reddy, *J. Mater. Sci. Technol.*, 2013, **29**, 647-651.
2. M. Majumder, I. Biswas, S. Pujaru, A.K. Chakraborty, *Thin Solid Films*, 2015, **589**, 741-749.
3. R. Lopez, R. Gomez, *J. Sol-Gel Sci. Technol.*, 2012, **61**, 1-7.