Supplementary Information

Cu:NiO as a hole-selective back contact to improve the photoelectrochemical performance of CuBi$_2$O$_4$ thin film photocathodes

Angang Song, Paul Plate, Abdelkrim Chemseddine, Fuxian Wang, Fatwa F. Abdi, Markus Wollgarten, Roel van de Krol, and Sean P. Berglund

b. Institute für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany
c. Department Nanoscale Structures and Microscopic Analysis, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
* E-mail: sean.berglund@helmholtz-berlin.de

Figure S1. LSV scans for CuBi$_2$O$_4$ films on FTO and FTO/Cu:NiO (7 nm) at a thicknesses of 260 nm measured in 0.3 M K$_2$SO$_4$ and 0.2 M phosphate buffer (pH 6.65) with H$_2$O$_2$ added as an electron scavenger under backside and frontside illumination.
Figure S2. (a) LSV scans for FTO/CuBi$_2$O$_4$ and (b) FTO/Cu:NiO (7 nm)/CuBi$_2$O$_4$ films at different film thicknesses measured in 0.3 M K$_2$SO$_4$ and 0.2 M phosphate buffer (pH 6.65) with H$_2$O$_2$ added as an electron scavenger under backside illumination.
Figure S3. LSV scans for Cu: NiO at a thicknesses of 34 nm measured in 0.3 M K$_2$SO$_4$ and 0.2 M phosphate buffer (pH 6.65) with Ar bubbling and with H$_2$O$_2$ under backside illumination.

Figure S4. LSV scans for CuBi$_2$O$_4$ films (~260 nm) based on different film thicknesses of Cu: NiO (7, 34, and 102 nm) measured in 0.3 M K$_2$SO$_4$ and 0.2 M phosphate buffer (pH 6.65) with H$_2$O$_2$ under backside illumination.
Figure S5. IPCE spectra of CuBi$_2$O$_4$ on FTO (blue dot line), CuBi$_2$O$_4$ on Cu:NiO (red and green dot line). The measurements were performed in 0.3 M K$_2$SO$_4$ and 0.2 M phosphate buffer (pH 6.65) with H$_2$O$_2$ under backside illumination.

Figure S6. Power spectra for back illumination IPCE measurements.
Figure S7. Constant potential measurement at 0.6 V vs RHE for 260 nm CuBi$_2$O$_4$ films based on bare FTO and 7 nm Cu:NiO in the dark and light (AM1.5 irradiation). Measurements were done in 0.3 M K$_2$SO$_4$ and 0.2 M phosphate buffer (pH 6.65) with Ar bubbling and with H$_2$O$_2$ under backside illumination.

Figure S8. Absorptance spectra for bare FTO, FTO/Cu:NiO (7nm) and FTO/CuBi$_2$O$_4$ and FTO/Cu:NiO (7nm)/CuBi$_2$O$_4$. 
Figure S9. (a) Transflectance spectra and (b) direct bandgap Tauc plots for Cu: NiO thin films with different thicknesses (7, 34, and 102 nm) deposited on glass substrates and (c) direct band gap Tauc plot of FTO substrate.
Figure S10. AFM images of (a) bare FTO, and (b) a 7 nm Cu:NiO layer, and (c) a 34 nm Cu:NiO layer deposited on FTO.
Figure S11. Top-view SEM image of 260 nm CuBi$_2$O$_4$ deposited on FTO and corresponding EDX elemental mapping of (b) Cu, (c) Bi, (d) O and (d) Sn.
Figure S12. Top-view SEM image of 7 nm Cu:NiO thin film deposited on FTO and corresponding EDX elemental mapping of (b) Cu, (c) Bi, (d) O, and (e) Sn.
Figure S13. (a) Drawing of the laser cut pattern used for solid-state I-V measurements. (b) SEM image of an FTO substrate with a laser cut.
Figure S14. Schematics of the (a) FTO/glass/FTO, (b) FTO/CuBi$_2$O$_4$/FTO, (c) FTO/Cu:NiO/FTO, and (d) FTO/Cu:NiO/CuBi$_2$O$_4$/Cu:NiO/FTO samples used for solid-state I-V measurements. The CuBi$_2$O$_4$ and Cu:NiO thicknesses were 260 and 7 nm, respectively.
Figure S15. Schematic illustrating the band bending of back-to-back Schottky barriers (FTO/CuBi$_2$O$_4$/FTO sample) at (a) V = 0 V and (b) V ≠ 0 V.

**Derivation of Equation for Back-to-Back Schottky Diodes**

The current densities across back-to-back Schottky barriers, $J_1$ and $J_2$ (A/cm$^2$), are governed by the following equations:

\[
J_1 = A^* T^2 \exp \left( \frac{-q \phi_{Beff1}}{kT} \right) \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]
\]

\[
J_1 = J_{s1} \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]
\]

\[
J_2 = -A^* T^2 \exp \left( \frac{-q \phi_{Beff2}}{kT} \right) \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]
\]

\[
J_2 = -J_{s2} \left[ \exp \left( \frac{-qV}{kT} \right) - 1 \right]
\]

$A^*$ is the reduced effective Richardson Constant (A cm$^{-2}$ K$^{-2}$), $T$ is the temperature (K), $q$ is the electronic charge ($1.602 \times 10^{-19}$ C), $k$ is the Boltzmann constant ($1.381 \times 10^{-23}$ m$^2$ kg s$^{-2}$ K$^{-1}$), $\phi_{Beff1}$ and $\phi_{Beff2}$ are the effective barrier heights (eV), $V$ is the overall applied voltage (V), and $V_1$ and $V_2$ are resulting voltages at each back-to-back Schottky barrier (V).

From continuity and symmetry, the overall current density ($J$) and applied voltage ($V$) are related to the individual values as follows:
\[ J = J_1 = J_2 \]

\[ V = V_1 + V_2 \]

Substitution of variables can be used to solve for \( J \).

\[ V_1 = \frac{kT}{q} \ln \left[ 1 + \frac{J}{J_{s1}} \right] \]

\[ V_2 = -\frac{kT}{q} \ln \left[ 1 - \frac{J}{J_{s2}} \right] \]

\[ V = \frac{kT}{q} \ln \left[ 1 + \frac{J}{J_{s1}} \right] - \frac{kT}{q} \ln \left[ 1 - \frac{J}{J_{s2}} \right] \]

\[ J = \frac{J_{s1} J_{s2} \exp \left( \frac{qV}{2kT} \right) - J_{s1} J_{s2} \exp \left( -\frac{qV}{2kT} \right)}{J_{s1} \exp \left( \frac{qV}{2kT} \right) + J_{s2} \exp \left( -\frac{qV}{2kT} \right)} \]

\[ J = \frac{J_{s1} J_{s2} \sinh \left( \frac{qV}{2kT} \right)}{J_{s1} \exp \left( \frac{qV}{2kT} \right) + J_{s2} \exp \left( -\frac{qV}{2kT} \right)} \]

Under the assumption that the barrier height of each Schottky barrier, scales linearly with the applied voltage, the effective barrier heights can be defined in terms of the ideality factors, \( n_1 \) and \( n_2 \).

\[ \phi_{B_{\text{eff}1}} = \phi_{B_{01}} + V_1 \left( 1 - \frac{1}{n_1} \right) \]

\[ \phi_{B_{\text{eff}2}} = \phi_{B_{02}} - V_2 \left( 1 - \frac{1}{n_2} \right) \]

\( \phi_{B_{01}} \) and \( \phi_{B_{02}} \) are the barrier heights at zero bias (eV).
\[ J = \frac{2 A^{**} T^2 \exp \left(-\frac{q \left[ \phi_{B01} + V_1 \left(1 - \frac{1}{n_1} \right) \right]}{kT}\right) A^{**} T^2 \exp \left(-\frac{q \left[ \phi_{B02} - V_2 \left(1 - \frac{1}{n_2} \right) \right]}{kT}\right) \sinh \left(\frac{qV}{2kT}\right)}{A^{**} T^2 \exp \left(-\frac{q \left[ \phi_{B01} + V_1 \left(1 - \frac{1}{n_1} \right) \right]}{kT}\right) \exp \left(\frac{qV}{2kT}\right) + A^{**} T^2 \exp \left(-\frac{q \left[ \phi_{B02} - V_2 \left(1 - \frac{1}{n_2} \right) \right]}{kT}\right) \exp \left(-\frac{qV}{2kT}\right)} \]

By the symmetry of the system the back-to-back Schottky diodes should have similar barrier heights at zero bias and ideality factors.

\[ \phi_{B01} = \phi_{B02} = \phi_B \]

\[ n_1 = n_2 = n \]

Furthermore, if the channel resistance is low, then voltages at each Schottky barrier can be assumed to be equal.

\[ V_1 = V_2 = \frac{V}{2} \]

\[ J = \frac{2 A^{**} T^2 \exp \left(-\frac{2q \phi_B}{kT}\right) \exp \left(-\frac{q(V - V)}{2kT}\right) \exp \left(-\frac{q(V - V)}{2nkT}\right) \sinh \left(\frac{qV}{2kT}\right)}{\exp \left(-\frac{q \phi_B}{kT}\right) \exp \left(-\frac{qV}{2kT}\right) \exp \left(\frac{qV}{2nkT}\right) + \exp \left(-\frac{qV}{2nkT}\right) \exp \left(-\frac{qV}{2kT}\right)} \]

\[ J = \frac{2 A^{**} T^2 \exp \left(-\frac{2q \phi_B}{kT}\right) \sinh \left(\frac{qV}{2kT}\right)}{\exp \left(\frac{qV}{2nkT}\right) + \exp \left(-\frac{qV}{2nkT}\right)} \]

\[ J = \frac{A^{**} T^2 \exp \left(-\frac{2q \phi_B}{kT}\right) \sinh \left(\frac{qV}{2kT}\right)}{\cosh \left(\frac{qV}{2nkT}\right)} \]

References


Figure S16. Current density vs. voltage (J-V) measurements at different temperatures for (a) FTO/CuBi$_2$O$_4$/FTO and (b) FTO/Cu:NiO/FTO samples with J fit lines included.

Figure S17. Electrochemical impedance spectroscopy (EIS) at 1.00 V vs. RHE for (a) CuBi$_2$O$_4$ deposited on FTO, (b) CuBi$_2$O$_4$ (260 nm) deposited on Cu:NiO (7 nm) on FTO, (c) Cu:NiO (34 nm) deposited on FTO, and (d) bare a FTO substrate. The measurements were performed in 0.3 M K$_2$SO$_4$ and 0.2 M phosphate buffer (pH 6.65). Note that above 1 kHz, the real part of the impedance is constant, whereas the imaginary part has a slope of -1. This implies that the system behaves as a resistance in series with a pure capacitance, which is a prerequisite for Mott-Schottky analysis.
(a) FTO/Cu: NiO/CuBi$_2$O$_4$

$\phi_{fb} = 1.17 \text{ V}_{RHE}$

$N_A = 3.4 \times 10^{19} \text{ cm}^{-2}$

(b) Bare FTO

$\phi_{fb} = 0.305 \text{ V}_{RHE}$
Figure S18. Mott–Schottky plots obtained for CuBi$_2$O$_4$ films and bare FTO. (a) Mott–Schottky of CuBi$_2$O$_4$ films deposited on 7 nm Cu:NiO film (b) Mott–Schottky of bare FTO. UPS cutoff spectra measured without bias for (c) CuBi$_2$O$_4$ and (d) Cu:NiO thickness of 34 nm deposited on FTO substrates and UPS cutoff spectra measured with a 2 V bias for a bare FTO substrate. Mott–Schottky measurements were performed in 0.3 M K$_2$SO$_4$ and 0.2 M phosphate buffer (pH 6.65) at 5 kHz, 7 kHz, and 9 kHz.
Figure S19. Electrochemical impedance spectroscopy (EIS) performed under backside illumination at 1.1 V vs. RHE for CuBi$_2$O$_4$ films deposited on FTO (black circle line) and 7 nm Cu:NiO layer (red square line).

Table S1. Summarizing Energy Levels

| Material   | Band Gap, $E_g$ (eV) | Flat-Band Potential, $\phi_{fb}$ (eV / V vs. RHE) | Work Function, WF (eV / V vs. RHE) | Average, $E_F$ ($\phi_{fb}$ & WF) (eV / V vs. RHE) | n-type $N_A$ (cm$^{-3}$) | p-type $N_D$ (cm$^{-3}$) | $|E_F - E_V|$ (eV) | Valence Band Offset ($|E_F - E_F|$) |
|------------|----------------------|---------------------------------|-------------------------------|---------------------------------|---------------------------|---------------------------|-------------------|---------------------------|
| FTO        | 3.7                  | 4.81 / 0.31                     | 4.61 / 0.11                   | 4.71 / 0.21                     | $1 \times 10^{21}$       |                          | 0.36              |                           |
| Cu:NiO     | 3.75                 | 5.21 / 0.71                     | 5.11 / 0.61                   | 5.16 / 0.66                     | $4.6 \times 10^{18}$     | $< 0.077$                 | 0.36              |                           |
| CuBi$_2$O$_4$ | 1.6                | 5.62 / 1.12                     | 5.79 / 1.29                   | 5.71 / 1.21                     | $3.2 \times 10^{18}$     | $< 0.077$                 | 0.19              |                           |

Table S2. Sheet resistance of different thickness of Cu:NiO thin films deposited on glass substrates.

<table>
<thead>
<tr>
<th>As Deposited Thickness (nm)</th>
<th>Post Anneal Thickness (nm)</th>
<th>Film Sheet Resistance ($\Omega/\square$)</th>
<th>Film Resistivity ($\Omega$ m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4</td>
<td>7</td>
<td>$1.16 \times 10^9$</td>
<td>0.815</td>
</tr>
<tr>
<td>12</td>
<td>34</td>
<td>$9.58 \times 10^7$</td>
<td>3.258</td>
</tr>
<tr>
<td>66</td>
<td>102</td>
<td>$8.33 \times 10^7$</td>
<td>8.492</td>
</tr>
</tbody>
</table>