Electronic Supporting Information

Extracting Large photovoltages from a-SiC Photocathodes with an Amorphous TiO$_2$ Front Surface Field Layer for Solar Hydrogen Evolution

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1 Electrochemical Impedance Spectroscopy

1.1 a-SiC photocathodes

The flat band potential ($V_{fb}$) and the acceptor concentration ($N_A$) of the (p/i) a-SiC photocathode was characterized by the electrochemical impedance spectroscopy (EIS) and was estimated using the Mott-Schottky relationship\(^1\):

$$\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_0 \varepsilon_r e N_A} \left( V - V_{fb} - \frac{kT}{e} \right)$$

Eq. 1

In this equation, $C_{SC}$ is the space charge capacitance density, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the relative permittivity of a-SiC (14)\(^2\), $e$ is the electron the charge, $A$ is the active surface area (0.283 cm\(^2\)), $k$ is the Boltzmann’s constant and $T$ is the temperature (298). Figure 1 shows the Mott-Schottky plot of the (p/i) a-SiC at chosen frequency 0.5 kHz.

![Mott-Schottky plot](image)

**Figure S1** Mott-Schottky plot of the (p/i) a-SiC at 5 kHz taken in the dark.

The $V_{fb}$ can be obtained from intercept between the extrapolated linear line and x-axis of the Mott-Schottky plot, which is estimated to be ~0.98 V vs. RHE. Using the Eq. 1 the $N_A$ of the
is approximated to be $9.69 \times 10^{17} \text{cm}^{-3}$. The valence band edge $E_V$ position can be determined using the following relationship:

$$E_F - E_V = -\frac{kT}{e} \ln \left( \frac{N_A}{N_V} \right)$$

Eq. 2

The density of valance band states ($N_V$) can be obtained using the following equation:

$$N_V = 2\left( \frac{2\pi m^*_h kT}{\hbar^2} \right)^{3/2}$$

Eq. 3

where the effective mass of hole ($m^*_h$) of $0.3m_0$ is assumed to be the same to that of c-Si. Using the above formula, the $N_V$ is calculated to be $4.08 \times 10^{18} \text{cm}^{-3}$. This suggests that the Fermi level is positioned at 36.94 mV above the valence band edge.

1.2 TiO$_2$

![Mott-Schottky plots of TiO$_2$ films deposited onto FTO glass substrate at various temperatures measured at a frequency of 500 Hz. The intersection of the extrapolated linear line with the x-axis represents the $V_{fb}$ and the difference in slopes reflects the variation in the donor density. All measurements were performed in 0.5 M potassium hydrogen phthalate (pH 4) electrolyte solution.](image)

The donor density ($N_D$), the effective mass of density of states in the conduction band ($N_C$) and the position of the Fermi level relative to the conduction band of TiO$_2$ ($E_{CB}-E_F$) were calculated using the equations in the main paper and are summarized in Table S1.

Table S1 The electronic properties of TiO$_2$ as obtained from the Mott-Schottky results.
<table>
<thead>
<tr>
<th>$n$-type</th>
<th>$E_{fb}$ (V/RHE)</th>
<th>$N_C$ (cm$^{-3}$)</th>
<th>$N_D$ (cm$^{-3}$)</th>
<th>$E_{CB-E_F}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (120 °C)</td>
<td>−0.06</td>
<td>$7.86 \times 10^{20}$</td>
<td>$1.30 \times 10^{20}$</td>
<td>46.12</td>
</tr>
<tr>
<td>TiO$_2$ (150 °C)</td>
<td>−0.11</td>
<td>$7.86 \times 10^{20}$</td>
<td>$1.56 \times 10^{20}$</td>
<td>41.44</td>
</tr>
<tr>
<td>TiO$_2$ (170 °C)</td>
<td>−0.15</td>
<td>$7.86 \times 10^{20}$</td>
<td>$1.96 \times 10^{20}$</td>
<td>35.71</td>
</tr>
<tr>
<td>TiO$_2$ (200 °C)</td>
<td>−0.2</td>
<td>$7.86 \times 10^{20}$</td>
<td>$2.61 \times 10^{20}$</td>
<td>28.32</td>
</tr>
</tbody>
</table>

From Table S1, it is apparent that TiO$_2$ deposited at different temperatures do not show significant variations of $V_{fb}$ and $N_D$. Seger et al. reported that TiO$_2$ still allowed effective electron transport in the conduction even with low electron density ($10^{17}$). Since our ALD TiO$_2$ already show very high electron density, no further attempt to increase the deposition temperature nor vacuum annealing to improve the conductivity of the film.

2 Optical band gap

![Figure S3](image)

**Figure S3** Tauc plot of the a-SiC based on the refractive indices ($n$ & $k$) measured using the spectroscopy ellipsometry. The interception between the extrapolated linear line and the x-axis represents the direct optical band gap. The band gap of a-SiC and TiO$_2$ are 2 eV and 3.25 eV, respectively.

3 Solar photocurrent & irradiance spectra

The solar photocurrent is obtained by the multiplication of the IPCE spectrum with the spectral irradiance$^5$ of the ASTM AM1.5G$^6$ (1000W/m$^2$):

$$I(\lambda) = IPCE \cdot E(\lambda) \cdot \lambda \cdot e/\hbar c$$

Eq. 4
where $I(\lambda)$ is the solar photocurrent spectrum, $E(\lambda)$ is the spectral irradiance of the ASTM AM1.5G, $h$ is the Planck’s constant and $c$ is the speed of light in vacuum. The total photocurrent of the photocathode under ASTM AM1.5G illumination is obtained by the integration over the spectrum:

$$J_{ASTM\, AM1.5G} = \int I(\lambda) d(\lambda)$$

**Eq. 5**

**Figure S4** Solar photocurrent spectra of the (p/i) a-SiC (green solid line) and the (p/i) a-SiC/(n) TiO$_2$ (solid blue line) photocathodes at 0 V vs. RHE and the integrated photocurrent of the corresponding photocathodes (dash lines) at the same wavelengths.

Using Eq. 5 the solar photocurrent of the (p/i) a-SiC and the (p/i) a-SiC/(n) TiO$_2$ photocathodes can be calculated, that are 1.72 mA cm$^{-2}$ and 10.96 mA cm$^{-2}$, respectively.
Figure S5  Irradiance spectra of the solar simulator Xe lamp used for $j-V$ measurements (red line) and the ASTM AM1.5G (black line).
4 \(j-V\) characteristics

**Figure S6** Illuminated \(j-V\) characteristics of the Ni-Mo coated (p/i) a-SiC photocathode before (green line) and after stability (purple line) test and after Ni-Mo redeposition (red dash line) measured in a 0.5 M potassium hydrogen phthalate electrolyte at pH 4.

**Figure S7** dark \(j-V\) characteristics of the FTO coated by TiO\(_2\) and TiO\(_2\)/Ni-Mo in potassium hydrogen phthalate solution at pH 4. The TiO\(_2\) was deposited at 150 °C. The FTO/Ni-Mo/TiO\(_2\) shows nearly zero overpotential for hydrogen evolution reaction as indicated by the \(V_{onset}\) of 0 V vs. RHE.
5 SEM image and photograph

**Figure S8** Cross-sectional SEM image of the (p/i) a-SiC/(n) TiO$_2$, showing the approximate thickness of the film.

**Figure S9** Photograph of the (p/i) a-SiC and the (p/i) a-SiC/(n) TiO$_2$ samples.
Figure S10  a) Top-view SEM image of the (p/i) a-SiC/(n) TiO₂ and b) the magnification of Figure S10a

Figure S11  a) Top-view SEM image of the (p/i) a-SiC/(n) TiO₂/Ni-Mo and b) the magnification of Figure S11a
Figure S12 Top-view SEM image of the (p/i) a-SiC/(n) TiO$_2$/Ni-Mo after chronoamperometry measurement for 12 hours.

References


