Supplementary Information

Selenylation to charge transfer improvement at the counter electrode (CE)/electrolyte interface for nanocrystalline Cu$_{1.8}$S$_{1.8}$Se$_x$ CEs

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1. Synthesis of nanocrystalline Cu$_{1.8}$S and Cu$_{1.8}$S$_{1-x}$Se$_x$ and fabrication of the CEs

The reaction in the preparation of Cu$_{1.8}$S can be expressed as follows [1]:

\[
2\text{CuCl}_2 + \text{CH}_4\text{N}_2\text{S} + \text{H}_2\text{O} \rightarrow 2\text{CuCl} + \text{S} + 2\text{HCl} + \text{NH}_2\text{CONH}_2
\]

\[
\text{CH}_4\text{N}_2\text{S} + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{NH}_4^+ + \text{CO}_3^{2-}
\]

\[
\text{Cu}^{2+} + \text{H}_2\text{S} \rightarrow \text{CuS} + 2\text{H}^+
\]

\[
8\text{CuCl} + \text{CuS} + 4\text{H}_2\text{S} \rightarrow \text{Cu}_3\text{S}_5 + 8\text{HCl}
\]
2. XRD patterns of the Cu$_{1.8}$S$_{1-x}$Se$_x$ CEs prepared by nanocrystalline Cu$_{1.8}$S$_{1-x}$Se$_x$ powder

![XRD patterns of CEs](image)

**Figure S2.** XRD patterns of the CEs of F-S$_0$, F-S$_{01}$, F-S$_{02}$ and F-S$_{03}$.

After annealing at 250 °C for 30 min, in addition to the peaks distinct in the precursor powder, Cu$_2$S arises in F-S$_0$. During the annealing, partial S was evaporated and the relatively rich Cu in the lattice together with the remaining S formed the Cu$_2$S.
3. TEM images of the as-prepared powder samples of $S_0$ and $S_{02}$

![TEM images of $S_0$ and $S_{02}$](image)

*Figure S3. TEM images of $S_0$ and $S_{02}$.*

4. Specific surface areas of the powder samples of $S_0$ and $S_{02}$

![Specific surface area graphs](image)

*Figure S4. Adsorption and desorption curves of $S_0$ (a) and $S_{02}$ (b).*
5. The Valence band maximum (VBM) of the CEs

Figure S5. VB-XPS plots of the CEs F-S\textsubscript{0}, F-S\textsubscript{01}, F-S\textsubscript{02} and F-S\textsubscript{03}.

6. Properties of the Cu\textsubscript{1.8}S\textsubscript{1-x}Se\textsubscript{x} CEs prepared by selenylation of Cu\textsubscript{1.8}S films

6.1 Selenylation of Cu\textsubscript{1.8}S films to Cu\textsubscript{1.8}S\textsubscript{1-x}Se\textsubscript{x} CEs

In this process, Cu\textsubscript{1.8}S\textsubscript{1-x}Se\textsubscript{x} CEs were prepared by selenylation of Cu\textsubscript{1.8}S films fabricated using the same process depicted in the manuscript, that is, Cu\textsubscript{1.8}S films were first spin-coated onto FTO surfaces. Then, different amounts of selenium powder (0 mg, 50 mg, 100 mg, 150 mg) were added during the film annealing process for selenylation at 550 °C for 15 min under nitrogen atmosphere. The CEs were named as F-CS\textsubscript{0}, F-CS\textsubscript{1}, F-CS\textsubscript{2}, F-CS\textsubscript{3}, respectively. Schematic diagram of the fabrication
of the CEs are shown in Fig. S4.

**Figure S6.** Schematic diagram of the fabrication of Cu$_{1.85}$S$_1$Se$_x$ CEs.

### 6.2 Optical properties

The optical absorption of the F-CS$_0$, F-CS$_1$, F-CS$_2$ and F-CS$_3$ CEs are shown in Fig. S5a. The CEs showed good absorption in the visible range. The Tauc plotting method was adopted to estimate the bandgap values of the samples. As shown in Fig. S5b, with the increasing of the selenylation degree, the bandgap decreases firstly and then increases. This indicate that proper selenylation degree can modulate the bandgap of the material [2].

**Figure S7.** Absorbance spectra (a) and bandgap of the CEs (b).
6.3 Energy level alignment in the DSSCs

Figure S6a-6d shows the VBM values estimated by VB-XPS. As shown in Fig. S6e, ΔE is the difference between the conduction band bottom (CBB) values of the F-CS₂, F-CS₂, F-CS₂ and F-CS₃ CEs and redox potential of the electrolyte (E_R/R') (-4.9 eV) which can be used to evaluate the driving force for charge transfer at the CE/electrolyte interface. ΔE is in the order of F-CS₂ > F-CS₃ > F-CS₁ > F-CS₀.

**Figure S8.** VB-XPS plots of CEs (a-d) and Energy level alignment in the DSSCs (e).
6.4 Photovoltaic performances of the DSSCs

Figure S7 shows the J-V curves and corresponding parameters of the DSSCs. The PCE gradually increased with increasing selenylation, and when F-C\textsubscript{S\textsubscript{2}} was used as CE of DSSCs, the values of both $J_{sc}$ and $FF$ improved and the PCE increased to 4.16%, which was higher than that of the Cu\textsubscript{1.8}S (2.87%). With a further increase in selenylation, the PCE and $FF$ present a decreasing trend (F-CS\textsubscript{3}) [3]. The PCE of F-CS\textsubscript{0} is lower than that of F-S\textsubscript{0} (3.38%), which is due to the increase in FTO conductive glass resistivity during the annealing of F-CS\textsubscript{0} at 550 °C [4, 5].

![Photocurrent density voltage characteristic graphs of DSSCs.](image)

**Figure S9.** Photocurrent density voltage characteristics of DSSCs.

6.5 Electrochemical characterization

The Nyquist plots of the DSSCs are shown in Fig. S8 and the parameters are summarized in Table S1. The overall decrease in $R_s$ values after selenylation indicates
that selenylation of Cu$_{1.8}$S can effectively improve the electrical conductivity of Cu$_{1.8}$S. The $R_{ct}$ of F-CS$_2$ is the smallest among the samples, indicating that charge transfer at the F-CS$_2$/electrolyte interface has the highest rate compared with that in the cells with other CEs.

![EIS Nyquist plots of the DSSCs with the CEs.](image)

**Figure S10.** EIS Nyquist plots of the DSSCs with the CEs.

<table>
<thead>
<tr>
<th>CE</th>
<th>$R_s$ (Ω·cm$^2$)</th>
<th>$R_{ct}$ (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-CS$_0$</td>
<td>27.9</td>
<td>27.3</td>
</tr>
<tr>
<td>F-CS$_1$</td>
<td>16.5</td>
<td>21.5</td>
</tr>
<tr>
<td>F-CS$_2$</td>
<td>16.4</td>
<td>13.0</td>
</tr>
<tr>
<td>F-CS$_3$</td>
<td>19.2</td>
<td>28.5</td>
</tr>
</tbody>
</table>

Table S1. EIS parameters extracted from Fig. S8.
6.6 Stability of the as-fabricated CEs

![Graphs and images](image)

**Figure S11.** CA curves of CEs (a for F-S02 and b for F-CS2), XRD pattern of F-SO2 before (F-S02) and after 1000 CV cycles (F-S’02) (c), and SEM image of F-SO2 surface after 1000 CV cycles.

**References**


