Supporting Information

A Cu$_2$Se-Cu$_2$O Film Electrodeposited on Titanium Foil as a Highly Active and Stable Electrocatalyst for the Oxygen Evolution Reaction

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Experimental Section

1. General chemicals and materials

All chemicals, including copper sulfate pentahydrate (CuSO$_4$•5H$_2$O), selenium dioxide (SeO$_2$), sodium bicarbonate (NaHCO$_3$), sodium hydroxide (NaOH), hydrochloric acid (HCl, ~37%) and Titanium foil (TF, thickness: 0.1 mm, purity: Ti $\geq$ 99.99%) were purchased from commercial suppliers and used without further purification. Milli-Q ultrapure water of 18.2 MΩ•cm was applied in all experiments.

2. Preparation of the Cu$_2$Se-Cu$_2$O/TF, Cu/TF, CuO/TF electrodes and the carbonate buffer solution

Firstly, TF substrates were sonicated in a 2.0 M HCl for 30 min to remove the surface oxides and pollutants, and rinsed subsequently with water and ethanol. The clean and bare TF substrates were obtained for next use after drying under 100 °C over 2 h. The Cu$_2$Se-Cu$_2$O/TF electrodes were prepared according to the following steps. The anodes were formed by the electrodeposition method, which was carried out in an aqueous solution (50 mM CuSO$_4$•5H$_2$O and 25 mM SeO$_2$) from a conventional three-electrode configuration with a TF substrate as the working electrode, saturated Ag/AgCl as the reference electrode, and Pt mesh as the auxiliary electrode. Electrodeposition was conducted by controlled potential electrolysis at -0.65 V (vs. Ag/AgCl) for 600 s at room temperature. After deposition, the Cu$_2$Se-Cu$_2$O/TF electrode was rinsed with deionized water thoroughly. The Cu/TF electrodes were prepared by the similarly electrodeposited method without using Se precursor (SeO$_2$). The CuO/TF electrodes were obtained via calcination of the Cu/TF electrodes at 350 °C for 3 h in the air. The carbonate buffer solution (0.2 M, pH 11.0) as electrolyte for electrochemical measurements was prepared by dissolving NaHCO$_3$ (0.2 M) in ultrapure water and the pH value of the solution was adjusted to 11.0 by NaOH (solid).

3. The characterization of the electrodes

The scanning electron microscopy (SEM) images, the energy-dispersive X-ray (EDX) spectrum analysis and elemental distributions mapping were taken with a FEI Nova Nano SEM 450 instrument (3 kV) equipped with the energy-dispersion X-ray fluorescence analyzer. Transmission electron
microscopy (TEM) images and higher-resolution transmission electron microscopy (HRTEM) images were obtained with FEI TF30 equipment. The X-ray diffraction (XRD) patterns of the electrodes were recorded by D/max-2400 diffractometer with Cu-Kα radiation source. The measurement was performed from 10° to 80° with a scan-rate of 8 °/min. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo VG ESCALAB 250X using Al Kα radiation as the excitation source. The binding energy was calibrated according to C 1s neutral carbon peak at 284.8 eV.

4. Electrochemical measurements

All electrochemical experiments were carried out using a CHI Instruments Electrochemical Analyzer (CHI 660E) at room temperature (25 ± 2 °C). The water oxidation performance of the Cu$_2$Se-Cu$_2$O/TF electrode was estimated from linear scan voltammetry (LSV) plots while the stability of the catalyst was studied by chronopotentiometry method. The electrochemical measurements were performed in a three-electrode system: the Cu$_2$Se-Cu$_2$O/TF electrode, the Ag/AgCl electrode and Pt mesh as work electrode, reference electrode and counter electrode, respectively. The reference electrode was calibrated by Ru(bpy)$_3$ (1.26 V vs. NHE) before using. The 100% iR-corrected was applied in the LSV and chronopotentiometry experiments. All the potentials were displayed versus reversible hydrogen electrode (RHE) by: $E_{(RHE)} = E_{(Ag/AgCl)} + 0.191 + 0.059 \times pH$. All of the current density in this paper was calculated based on the geometric area of electrode. The LSV measurements were executed under the scan rate of 5 mV/s. Moreover, the chronopotentiometry experiment was performed at a constant current density of 10 mA/cm$^2$ under gently stirring. At last, the Faradaic efficiency of the Cu$_2$Se-Cu$_2$O/TF electrode was carried out in a single gas-tight cell (total volume of 126 mL) equipped with Cu$_2$Se-Cu$_2$O/TF electrode (1.0 cm$^2$ active area) as the working electrode, Ag/AgCl as the reference electrode and Pt mesh as the counter electrode. The carbonate buffer electrolyte of 50.0 mL was added in electrolytic cell. Then, the electrolyte solution was degassed by bubbling Ar for 1 h to remove the air. Then the electrolysis was carried out at a stable current density of 10 mA/cm$^2$ without iR compensation in static electrolyte solution (0.2 M, pH = 11.0) for 2 h. The amount of evolved oxygen in the headspace was measured by gas chromatograph (GC 7890T instrument equipped with a thermal conductive detector) during electrolysis. The Faradic efficiency was calculated as $O_2(actual)/O_2(theoretical) \times 100\%$. The ECSA was determined by measuring the
capacitive current associated with double-layer charging from the scan-rate dependence of CVs. For this, the potential window of CVs was 1.39–1.49 V vs. RHE. The scan rates were 2, 4, 6, 8 and 10 mV/s. The double-layer capacitance ($C_{dl}$) was estimated by plotting the $\Delta J = (J_a - J_c)$ at 1.44 V vs. RHE against the scan rate. The linear slope is twice of the double-layer capacitance $C_{dl}$. Electrochemical impedance spectrum (EIS) was recorded at 1.84 V vs. RHE over a frequency range from $10^6$ to 0.1 Hz. In order to obtain the values of charge transfer resistances during OER, the Randles equivalent circuit method was used to fit experimental data. Here, $R_I$ is the resistance of the electrolyte; $CPE_1$ and $R_{ct}$ are the double-layer capacitance and charge transfer resistance, respectively, of the electrode in the electrolyte.

**Figure S1.** Photographs of the TF, Cu/TF, CuO/TF and Cu$_2$Se-Cu$_2$O/TF electrodes.
Figure S2. The SEM images of the bare TF (a) and Cu$_2$Se-Cu$_2$O/TF (b, c, d).

Figure S3. The SEM image (a) and EDX spectrum (b) of the Cu$_2$Se-Cu$_2$O/TF electrode. Elemental mapping images (c, d, e, f) of the corresponding elements in the Cu$_2$Se-Cu$_2$O/TF electrode.
**Figure S4.** The SEM images of the Cu/TF electrode.

**Figure S5.** The SEM images of the CuO/TF electrode.
Figure S6. The TEM images of the Cu$_2$Se-Cu$_2$O sample scraped from the Cu$_2$Se-Cu$_2$O /TF electrode.

Figure S7. Blank line: electrocatalytic activities of the Cu$_2$Se-Cu$_2$O/TF electrode (a graphite rod electrode was used during preparation of the electrode) using the graphite counter electrode in 0.2 M carbonate buffer solution buffer (pH = 11.0). Red line: electrocatalytic activities of the Cu$_2$Se-Cu$_2$O/TF electrode (Pt mesh electrode was used during preparation of the electrode) using the Pt counter electrode in 0.2 M carbonate buffer solution buffer (pH = 11.0).
Figure S8. The SEM images of Cu$_2$Se-Cu$_2$O/Ti foil after OER.

Figure S9. The powder XRD spectra of the Cu$_2$Se-Cu$_2$O materials before and after OER.

Figure S10. The TEM images of the Cu$_2$Se-Cu$_2$O sample scraped from the TF substrate after the OER.
Figure S11. The high-resolution XPS spectra of Cu 2p (a) and O 1s (b) of the Cu$_2$Se-Cu$_2$O/TF electrode after OER.

Figure S12. CV curves of the electrodes Cu/TF (a) and Cu$_2$Se-Cu$_2$O/TF (b) in 0.2 M carbonate buffer solution buffer (pH = 11.0) under different scan rates; (c) Plots of ic vs. scan rates v.
Figure S13. EIS spectra of the TF, Cu/T, CuO/TF and Cu$_2$Se-Cu$_2$O/TF electrode.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate</th>
<th>Electrolyte</th>
<th>pH</th>
<th>η (mV) @ the corresponding $i$ (mA/cm$^2$)</th>
<th>Ref.</th>
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<tr>
<td>Cu-bifunctional</td>
<td>FTO</td>
<td>0.1 M Bi buffer</td>
<td>9.2</td>
<td>749 mV @ 1.0 mA/cm$^2$</td>
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<tr>
<td>CuO nanowire</td>
<td>FTO</td>
<td>0.1 M Bi buffer</td>
<td>9.2</td>
<td>550 mV @ 1.0 mA/cm$^2$</td>
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<tr>
<td>CuO</td>
<td>Cu foil</td>
<td>1 M Na$_2$CO$_3$</td>
<td>10.8</td>
<td>580 mV @ 10.0 mA/cm$^2$</td>
<td>3</td>
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<tr>
<td>CuO from Cu-TEOA</td>
<td>ITO</td>
<td>0.1 M Ac buffer</td>
<td>12.4</td>
<td>780 mV @ 1.0 mA/cm$^2$</td>
<td>4</td>
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<tr>
<td>Cu$_2$S Nanoplate</td>
<td>GC</td>
<td>0.25 M Pi buffer</td>
<td>13.0</td>
<td>428 mV @ 10.0 mA/cm$^2$</td>
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<tr>
<td>CuO from Cu-en</td>
<td>ITO</td>
<td>0.2 M Pi buffer</td>
<td>12.0</td>
<td>550 mV @ 1.0 mA/cm$^2$</td>
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<tr>
<td>Leaf-type CuO</td>
<td>Cu foil</td>
<td>0.2 M Ci buffer</td>
<td>11.0</td>
<td>450 mV @ 10.0 mA/cm$^2$</td>
<td>7</td>
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<tr>
<td>CuO from Cu-Tris</td>
<td>ITO</td>
<td>0.2 M, Pi buffer</td>
<td>12.0</td>
<td>390 mV @ 1.0 mA/cm$^2$</td>
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<td>Cu(OH)$_2$</td>
<td>FTO</td>
<td>0.1 M Bi buffer</td>
<td>9.2</td>
<td>655 mV @ 1.0 mA/cm$^2$</td>
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<td>Cu$_2$Se-Cu$_2$O</td>
<td>Ti foil</td>
<td>0.2 M Ci buffer</td>
<td>11.0</td>
<td>465 mV @ 10.0 mA/cm$^2$</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: The η is overpential, the $i$ is the electrocatalytic current density, the FTO is fluorine-doped tin oxide glass, the ITO is indium tin oxide glass, the GC is glass carbon electrode. Bi is borate buffer solution, Pi is phosphate buffer solution, Ac is acetate buffer solution and Ci is carbonate buffer solution.
References