Electronic Supplementary Information

Efficient photoelectrochemical water oxidation enabled by an amorphous metal oxide-catalyzed graphene/silicon heterojunction photoanode

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Figure S1. Schematic process for the fabrication of Si/graphene/TiO$_2$/FeNiCoO$_x$ photoanode. (a) Si substrate with a 0.1 cm$^2$ exposed active area prepared by photolithography. (b) Graphene micro-net was transferred onto the Si substrate. (c) TiO$_2$ thin layer was deposited onto the Si/graphene substrate by ALD. (d) Si/graphene/TiO$_2$/FeNiCoO$_x$ photoanode obtained by deposition of FeNiCoO$_x$ film by a photochemical method.
Figure S2. (a) Photograph of the Si, Si/graphene and Si/graphene/TiO$_2$ electrode. (b) Photograph of an encapsulated electrode. (c) Schematic diagram to present the each layer of Si/graphene/TiO$_2$/FeNiCoO$_x$ electrode.
Figure S3. FE-SEM images of (a,b) graphene micro-net transferred onto Si substrate, (c,d) Si/graphene/TiO$_2$ (10 nm) structure, (e,f) Si/graphene/TiO$_2$ (50 nm) structure.
Figure S4. Cross-section SEM images of (a) 10 nm- and (b) 50 nm-TiO$_2$ thin films deposited on n-Si by ALD. XPS spectrum of Ti-2p peaks for the (c) 10 nm- and (d) 50 nm-TiO$_2$ thin films.

Figure S5. (a) Top-view and (b) cross-section SEM images of FeNiCoO$_x$ film deposited on FTO substrate.
Figure S6. X-ray photoelectron spectroscopy survey scan acquired on FeNiCoOx (a), FeNiOx (b) and FeCoOx (c) on FTO glass. (d) Fe, Co, and Ni 2p$_{3/2}$ regions of XPS spectra recorded on the three mixed-metal oxide films.
Figure S7. (a) Cyclic voltammograms (CVs) of FeNiCoOₓ, FeNiOₓ and FeCoOₓ films. (b) Tafel plots obtained for these films. (c) Current density versus applied voltage, without and with \( iR \) drop correction (plain and dash lines respectively) for the FeNiCoOₓ, FeNiOₓ and FeCoOₓ films. (d) Transmittance of the as prepared FeNiCoOₓ film and the film after operation at different potentials. (e) CVs of FeNiCoOₓ films prepared with different annealing time. (f) CVs of FeNiCoOₓ films prepared with different concentration. The thickness of the film increased with the increase in the total metal complex concentration.
Table S1. Overpotentials of the FeNiCoO<sub>x</sub>, FeNiO<sub>x</sub> and FeCoO<sub>x</sub> electrocatalysts.

<table>
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<tr>
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<th>FTO/FeNiCoO&lt;sub&gt;x&lt;/sub&gt; (7.5%, 100 °C)</th>
<th>FTO/FeNiO&lt;sub&gt;x&lt;/sub&gt; (7.5%, 100 °C)</th>
<th>FTO/FeCoO&lt;sub&gt;x&lt;/sub&gt; (7.5%, 150 °C)</th>
<th>FTO/FeNiCoO&lt;sub&gt;x&lt;/sub&gt; (7.5%, 200 °C)</th>
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<tr>
<td>Overpotential (mV) at 10 mA/cm&lt;sup&gt;2&lt;/sup&gt;</td>
<td>290±3</td>
<td>291±2</td>
<td>340±4</td>
<td>295±2</td>
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Table S2. Thickness, overpotential and transmittance of the FeNiCoO<sub>x</sub> film prepared with different total metal complex concentration and annealed at 100°C.

<table>
<thead>
<tr>
<th></th>
<th>Thickness (nm)</th>
<th>Overpotential (mV) at 10 mA/cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Transmittance (%) at 800 nm (1.5 V vs. RHE)</th>
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<tr>
<td>FTO/FeNiCoO&lt;sub&gt;x&lt;/sub&gt; (3%)</td>
<td>200±12</td>
<td>310±5</td>
<td>95.3±1.8</td>
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<tr>
<td>FTO/FeNiCoO&lt;sub&gt;x&lt;/sub&gt; (7.5%)</td>
<td>450±18</td>
<td>290±3</td>
<td>86.2±2.6</td>
</tr>
<tr>
<td>FTO/FeNiCoO&lt;sub&gt;x&lt;/sub&gt; (15%)</td>
<td>870±26</td>
<td>289±2</td>
<td>63.5±4.1</td>
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</table>

Figure S8. Open circuit voltage (OCV) measurement of Si/FeNiCoO<sub>x</sub>, Si/graphene/FeNiCoO<sub>x</sub> and Si/graphene/TiO<sub>2</sub>(10 nm)/FeNiCoO<sub>x</sub> photoanodes. The change of OCP in the dark and under illumination corresponding to the photovoltage of the photoanodes.
Figure S9. Current-voltage curves of non-annealed and annealed Si/graphene micro-net samples (a) in the dark and (c) under AM 1.5G illumination (100 mW/cm²). (b) is the diode ideality factor (n). The annealing of the Si/graphene samples were conducted in pure Ar ambient at 200 °C to 500 °C for 30 min. The diode ideality factor (n) presented in b is determined from the slope of the linear region of the forward-bias $\ln(I_{dark})$–$V$ characteristics through the relation: $n = \frac{q}{kT} \left( \frac{dV}{d(\ln I_{dark})} \right)$. n is the ideality factor that should be 1 if the Schottky junction current is purely from thermionic emission. For non-annealed Si/graphene micro-net devices, the diode ideality factor is greater than 2. The diode ideality factors decrease to 1.50 and 1.37 for the annealing temperature of 200 and 300 °C, respectively. When the annealing temperature increases further, the ideality factors increase again. The results suggest that the diode effect of devices with a mild temperature annealing (200 °C to 300 °C) becomes more desirable. However, annealing leads to a decreasing of the open-circuit voltage ($V_{OC}$), so annealing temperature of 200 °C could maintain a high $V_{OC}$ and a low n. Thus, we choose a deposition temperature of 200 °C during the TiO₂ deposition process.
Figure S10. Microscopy images of the Si/graphene/FeNiCoO\textsubscript{x} photoanode (a) before and (c) after stability test. Raman spectra taken at the region with graphene (b) before and (d) after stability test.
Figure S11. (a) Current-potential curves of Si/graphene/TiO$_2$ (10 nm)/FeNiCoO$_x$, Si/graphene/TiO$_2$ (50 nm)/FeNiCoO$_x$, Si/TiO$_2$ (10 nm)/FeNiCoO$_x$, and Si/TiO$_2$ (50 nm)/FeNiCoO$_x$ photoanodes in 1 M NaOH under AM 1.5G light illumination (Scan rate: 10 mV/s). (b) Current-potential curves of Si/TiO$_2$ (10, 50 nm)/FeNiCoO$_x$ photoanodes in 1 M NaOH under AM 1.5G light illumination. (c) Stability test of Si/TiO$_2$ (10, 50 nm)/FeNiCoO$_x$ photoanodes at 1.5 V vs. RHE.

Figure S12. The equivalent circuit used for the Nyquist plots of the Si-based photoanodes. The two semi-circles observed in the EIS spectra are ascribed to the solid/solid junction of the Si/graphene and the interface junction of the TiO$_2$/catalyst and/or TiO$_2$/electrolyte [S1,S2]. The charge transfer resistance at the interface junction of the Si/graphene/TiO$_2$/FeNiCoO$_x$ photoelectrode was measured to be ~330 Ω, which is much smaller than that of the Si/FeNiCoO$_x$ photoelectrode (~1700 Ω). The photoelectrode with a favorable Schottky junction can effectively enhance charge transfer from electrode surface to electrolyte.
Table S3. Fitting results obtained from EIS data of Figure 4(d).

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<thead>
<tr>
<th></th>
<th>$R_s$(Ω)</th>
<th>$R_{ss}$(Ω)</th>
<th>$R_{interface}$(Ω)</th>
<th>$CPE_{ss}$(F)</th>
<th>$CPE_{interface}$(F)</th>
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<tr>
<td>Si/FeNiCoO$_x$</td>
<td>17.6</td>
<td>33000.6</td>
<td>1700.4</td>
<td>3.5E-5</td>
<td>4.1E-6</td>
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<td>Si/graphene/FeNiCoO$_x$</td>
<td>30.1</td>
<td>160.5</td>
<td>400.5</td>
<td>9.4E-5</td>
<td>6.5E-6</td>
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<tr>
<td>Si/graphene/TiO$_2$(10nm)/FeNiCoO$_x$</td>
<td>53.9</td>
<td>211.5</td>
<td>330.2</td>
<td>3.8E-6</td>
<td>4.3E-6</td>
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</table>

Figure 13. Structure of (a) Si/FeNiCoO$_x$ and (b) Si/graphene/TiO$_2$/FeNiCoO$_x$ photoanodes and proposed energy band diagram in the dark (dark) and under light illumination (green). The band edges are assumed to be pinned at the solid/liquid interface. For the Si/FeNiCoO$_x$ structure, due to the permeable co-catalyst film and nonideality factors representing effects such as the surface states on Si surface, the built-in potential of Si/electrolyte solid/liquid junction is determined by the difference between the work function of Si ($\phi_{Si}$, ~4.3 eV) and the surface state energy level ($\phi_{ss}$). Therefore, a small band bending in Si was formed, which accounted for the low photovoltage (~100 mV). By introducing a graphene layer on Si, the barrier height of Si/graphene Schottky barrier is mainly defined by the difference between the work functions of Si ($\phi_{Si}$, ~4.3 eV) and graphene layer ($\phi_{graphene}$, ~4.8 eV) and thus the barrier height providing a large driving force for the PEC oxygen evolution. In this study, the higher photovoltage of ~420 mV observed on the photoanode with Si/graphene heterojunction indicates that an efficient solid/solid junction was formed. The high built-in field across the interface is favorable to the charge separation and transfer toward the Co-catalyst/electrolyte interface.
Figure S14. Current–time curves (held at 1.5 V vs. RHE) of Si/graphene/TiO$_2$/FeNiCoO$_x$ photoanodes with different TiO$_2$ thickness: (a) 10 nm; (b) 50 nm.

Figure S15. The plots for the amounts of the evolved gases (H$_2$ and O$_2$) for Si/graphene/TiO$_2$(10 nm)/FeNiCoO$_x$ recorded at 1.5 vs. RHE under illumination of 50 mW/cm$^2$ (100 W xenon lamp). A 1 M NaOH was used as an electrolyte. The blue and red lines in indicate the expected gas amounts of H$_2$ and O$_2$, respectively, calculated from the total charge recorded as the photocurrent.
Figure S16. Microscopy images of the Si/graphene/TiO$_2$/FeNiCoO$_x$ photoanode (a) before and (d) after stability test. Raman spectra taken at the region with graphene (b) before and (e) after stability test. (c) XPS spectrum of Ti-2p peak of Si/graphene/TiO$_2$ sample. (f) XPS spectrum of Ti-2p peak of Si/graphene/TiO$_2$/FeNiCoO$_x$ sample after stability test.
Figure S17. X-ray photoelectron spectroscopy survey scan acquired on Si/graphene/TiO$_2$ (10 nm)/FeNiCoO$_x$ before and after stability test.

Figure S18. (a-c) FE-SEM images of the Si/graphene/TiO$_2$ (10 nm)/FeNiCoO$_x$ photoanode after 3h stability test. (d-f) FE-SEM images of the Si/graphene/TiO$_2$ (50 nm)/FeNiCoO$_x$ photoanode after 3h stability test.
Figure S19. High resolution XPS spectra of (a) Fe-2p, (b) Ni-2p and (c) Co-2p peaks of the FeNiCoOₓ film on Si/graphene/TiO₂ electrode before and after stability test.

References: