Electronic Supplementary Information (ESI)

Photodeposition of a conformal metal oxide nanocoating

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Experimental Section

Sample synthesis: Cr$_2$O$_3$, Al$_2$O$_3$, ZnO, and In$_2$O$_3$ nanocoatings were photodeposited on GaN nanowires from an aqueous methanol solution containing the corresponding metal nitrate precursors in a Pyrex chamber with a quartz window. Cr(NO$_3$)$_3$·9H$_2$O (99.99%, Sigma Aldrich), Al(NO$_3$)$_3$·9H$_2$O (98%, Sigma Aldrich), Zn(NO$_3$)$_2$·6H$_2$O (98%, Sigma Aldrich) and In(NO$_3$)$_3$·5H$_2$O (99.999%, Strem Chemicals) were used as the precursors. Typically, the preparation conditions were as follows. First, GaN nanowires on Si wafer (~3 cm$^2$) was put in a Teflon holder and placed in the bottom of glass chamber. Next, 60 mL deionized water (purged with Ar for 10 min prior to the usage), 15 mL methanol, and 20 $\mu$L of 0.2 M metal nitrate (i.e., a concentration of 53.3 mM in the mixture solution) were added in the chamber. The chamber was then evacuated for 10 min and irradiated for 30 min using 300 W Xe lamp (2.6 W cm$^{-2}$, Excelitas Technologies) for the photodeposition of metal oxide nanocoating. GaN nanowires were grown on a 2-inch p-n junction Si wafer by plasma-assisted molecular beam epitaxy (MBE) under nitrogen-rich conditions as described previously.\(^1\) Prior to loading into the MBE chamber, Si wafer was cleaned with acetone, methanol and 10% buffered hydrofluoric acid to remove any organic contaminants and native oxides.

The synthesis procedure for Pt/Cr$_2$O$_3$/GaN/n$^+$–p Si sample was as follows: Cr$_2$O$_3$ nanolayer and Pt nanoparticles were photodeposited on GaN nanowires from an aqueous methanol solution in sequential order. The photodeposition process is similar to that described above, except for the use of 5 $\mu$L of 0.2 M Cr(NO$_3$)$_3$ and 15 $\mu$L of 0.2 M H$_2$PtCl$_6$ (99.9%, Sigma Aldrich) as precursors for the deposition of Cr$_2$O$_3$ and Pt, respectively.

The synthesis procedure for Cr$_2$O$_3$-coated TiO$_2$ sample was similar to that of Cr$_2$O$_3$-coated GaN, except for the use of TiO$_2$ on FTO (fluorine doped tin oxide) glass as the substrate and irradiated for 1 h. The TiO$_2$ on FTO was prepared by a drop casting method. 0.1 g TiO$_2$ particles (rutile, 99.9%, Sigma Aldrich) were dispersed ultrasonically in 50 mL ethanol, followed by dropping the suspension on FTO substrate and left the solvent evaporated overnight.

Characterization: Scanning electron microscopy (SEM) images were taken on an Inspect F-50 FE-SEM system at an accelerating voltage of 5 keV. Transmission electron microscopy
(TEM) images were acquired on FEI Tecnai G2 F20 microscope operated at 200 keV, with energy-dispersive X-ray spectroscopy (EDX) attached. The nanowires were scratched off from the Si substrate onto a copper grid prior to TEM measurements. X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Discovery X-ray diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were performed in a Thermo Scientific K-Alpha XPS system with a monochromatic Al Kα source (hν = 1486.6 eV). The binding energies were calibrated using adventitious C1s peak at 284.8 eV. Inductively coupled plasma–atomic emission spectroscopy (ICP-AES) analyses were conducted on a Thermo Scientific iCAP 6000 Series inductively coupled plasma–atomic emission spectroscopy instrument. The samples were digested in 5 ml aqua regia (HNO₃:HCl=1:3) at 95 °C for 3 h. Then the solution was diluted with an additional 5 mL demineralized water prior to the analysis. The NO₂⁻ content produced during the photodeposition was determined by a Varian Cary 50 UV–Vis spectrometer using a common Griess method.² Griess solution was prepared by dissolving 1 g Griess Reagent (G4410, Sigma-Aldrich) into 25 ml of ultrapure water. A calibration curve was obtained from commercial NaNO₂ of analytical standards (99.999%, Sigma Aldrich).

**Photoelectrochemical (PEC) measurements:** PEC experiments were conducted in 0.5 M H₂SO₄ solution with a three-electrode configuration and recorded using a potentiostat (Gamry Instruments, Interface 1000). GaN nanowires on p-n junction Si, Ag/AgCl and Pt wire were employed as the working electrode, reference electrode and counter electrode, respectively. A solar simulator (Newport Oriel) with an AM 1.5G filter was used as the light source, and the illumination intensity at the position of sample was calibrated to be 100 mW cm⁻². The scan rate of current-potential (J-V) curves was 20 mV/s. The recorded potentials versus Ag/AgCl were converted to versus RHE according to the following equation: \( E(\text{versus RHE}) = E(\text{versus Ag/AgCl}) + (0.0591 \times \text{pH}) + 0.1976 \), where 0.1976 is a conversion factor from the Ag/AgCl electrode to RHE at 25 °C. H₂ product from water splitting was detected by a gas chromatograph (GC, Shimadzu GC-8A) equipped with a thermal conducting detector (TCD), using high purity Ar as carrier gas.
The applied bias photon-to-current efficiency (ABPE) was calculated from $J-V$ curve using the following equation:

$$ABPE(\%) = \left[ \frac{J(\text{mA cm}^{-2}) \times (V_{\text{RHE}} - E^0)(V)}{P_\text{in}(\text{mW cm}^{-2})} \right] \times 100\%$$

where $J$ is the photocurrent density; $V_{\text{RHE}}$ is the applied potential vs. RHE; $E^0$ is the equilibrium water reduction potential in 0.5 M $\text{H}_2\text{SO}_4$ electrolyte, which is 0 V vs. RHE; $P_\text{in}$ is the incident illumination power density (AM 1.5G, 100 mW cm$^{-2}$).
Fig. S1. Top-view SEM images of (a) pristine GaN and (b) Cr$_2$O$_3$-deposited GaN.
Fig. S2. HRTEM image of Cr$_2$O$_3$-deposited GaN sample. It shows Cr$_2$O$_3$ coating layer is amorphous and GaN nanowire is single crystalline with the growth direction along the c-axis.
Fig. S3. XRD patterns of pristine GaN and Cr$_2$O$_3$-deposited GaN. The two samples display similar patterns attributed to GaN (002) peak. The (002) peak indicates the nanowire growth along the c-axis <0001> direction.
Fig. S4. XPS depth profile of survey spectrum in Cr$_2$O$_3$-deposited GaN sample as a function of etching time. As the etching time increased, the O 1s signal decreased progressively, and the N 1s signal increased progressively.
Fig. S5. Survey XPS spectrum of Cr$_2$O$_3$-deposited GaN sample. All the spectral features, except the common adventitious C 1s signal, are attributed to constituent element core-levels or Auger lines of Cr$_2$O$_3$-deposited GaN.
**Fig. S6.** EDX spectrum of Cr$_2$O$_3$-deposited GaN sample. The Cu signal arises from the TEM sample grid.
Fig. S7. TEM images of Cr$_2$O$_3$-deposited GaN samples with different coating thicknesses by varying the light illumination time of preparation: (a) 10 min, (b) 20 min, (c) 30 min and (d) 40 min. The Cr(NO$_3$)$_3$ precursor concentration was kept at 53.3 mM for the preparation of all the samples.
**Fig. S8.** XPS of Al 2p of Al$_2$O$_3$-deposited GaN sample. The Al 2p binding energy at 74.4 eV is assigned to Al$^{III}$ state from Al$_2$O$_3$.\(^3\)
Fig. S9. XPS of Zn 2p of ZnO-deposited GaN sample. The Zn 2p\textsubscript{3/2} binding energy at 1021.8 eV and Zn 2p\textsubscript{1/2} binding energy at 1044.9 eV are assigned to Zn\textsuperscript{II} state from ZnO.\textsuperscript{4}
Fig. S10. XPS of In 3d of In$_2$O$_3$-deposited GaN sample. The In 3d$_{5/2}$ binding energy at 444.5 eV and In 3d$_{3/2}$ binding energy at 452.0 eV are assigned to In$^{III}$ state from In$_2$O$_3$.\textsuperscript{5}
Fig. S11. Survey XPS spectrum of Al₂O₃-deposited GaN sample. All the spectral features, except the common adventitious C 1s signal, are attributed to constituent element core-levels or Auger lines of Al₂O₃-deposited GaN.
Fig. S12. EDX spectrum of Al$_2$O$_3$-deposited GaN sample. The Cu signal arises from the TEM sample grid.
Fig. S13. Survey XPS spectrum of ZnO-deposited GaN sample. All the spectral features, except the common adventitious C 1s signal, are attributed to constituent element core-levels or Auger lines of ZnO-deposited GaN.
**Fig. S14.** EDX spectrum of ZnO-deposited GaN sample. The Cu signal arises from the TEM sample grid.
Fig. S15. Survey XPS spectrum of In$_2$O$_3$-deposited GaN sample. All the spectral features, except the common adventitious C 1s signal, are attributed to constituent element core-levels or Auger lines of In$_2$O$_3$-deposited GaN.
Fig. S16. EDX spectrum of In$_2$O$_3$-deposited GaN sample. The Cu signal arises from the TEM sample grid.
Fig. S17. HRTEM images of (a) Al₂O₃ and (b) In₂O₃-deposited GaN samples, showing both Al₂O₃ and In₂O₃ coating layers are amorphous.
Fig. S18. XRD patterns of pristine GaN, $\text{Al}_2\text{O}_3$-deposited GaN and $\text{In}_2\text{O}_3$-deposited GaN. All samples display similar patterns attributed to GaN (002) peak.
Fig. S19. HRTEM image of ZnO-deposited GaN sample. It shows the crystallinity of ZnO coating layer.
Fig. S20. XRD patterns of pristine GaN and ZnO-deposited GaN. Despite the crystalline structure of ZnO, the (002) peak from ZnO overlaps that of GaN, because the lattice mismatch between the wurtzite ZnO (a = 3.249 Å and c = 5.207 Å) and wurtzite GaN (a = 3.190 Å and c = 5.189 Å) is as small as 0.4% in c-axis lengths. However, we cannot exclude the possibility that no noticeable detection of XRD peaks of crystalline ZnO may be due to its low amounts.
Fig. S21. XPS of Zn 2p of ZnO-deposited GaN samples prepared under dark and light irradiation.
**Fig. S22.** XPS of Zn 2p of ZnO-deposited GaN samples using different precursors. The added precursor concentration of zinc salts and NaNO₃ were 53.3 μM and 106.6 μM, respectively.
Fig. S23. HRTEM images of ZnO-deposited GaN samples using different precursors. (a) ZnSO₄, (b) ZnSO₄ + NaNO₃. It was found that there was no formation of ZnO nanocoating using ZnSO₄ as the precursor, whereas ZnO nanocoating was clearly observed using the combination of ZnSO₄ and NaNO₃ as the precursors.
**Fig. S24.** UV-visible spectra of mixtures of Griess solution and photodeposition solution after the preparation of ZnO-deposited GaN sample (1 mL Griess reagent + 10 ml sample solution). A sample solution prepared under dark condition is shown for comparison. Inset is the optical image of the mixture solution. The absorbance peak at 540 nm indicates the presence of NO$_2^-$ after the photodeposition process. The mechanism of the Griess reaction is a diazotization and coupling reaction as depicted below. NO$_2^-$ reacts with sulfanilamide (a) under acidic conditions to form the diazonium cation (b) which then couples to N-(1-naphthyl) ethylenediamine (c) for producing a red-violet colored azo dye (d), which strongly absorbs at 540 nm.
Fig. S25. (a) UV-visible spectra of mixtures of Griess solution and different concentrations of NaNO$_2$ (1 mL Griess reagent + 10 ml NaNO$_2$ solution). (b) The calibration curve of absorbance at wavelength of 540 nm versus NaNO$_2$ concentration. The absorbance at 540 nm of our NO$_2^-$ solution after the photodeposition of ZnO was measured to be 0.09, indicating a NO$_2^-$ concentration of 3.1 µM. Considering the solution volume of 75 mL, the produced NO$_2^-$ amount was calculated to be 0.23 µmol.
Fig. S26. Schematic of (a) reductive photodeposition and (b) oxidative photodeposition. CB: conduction band; VB: valence band; D: sacrificial electron donor; A: sacrificial electron acceptor.
Fig. S27. (a) SEM, (b) TEM, (c) HRTEM images, and EDX analysis of the edge (d) and center region (e) of Cr$_2$O$_3$-deposited TiO$_2$ particle. XPS depth profiles of (f) Cr 2p and (g) Ti 2p in Cr$_2$O$_3$-deposited TiO$_2$ as a function of etching time. SEM shows the TiO$_2$ particle sizes are in the range between 200 and 500 nm. It indicates Cr$_2$O$_3$ coated on TiO$_2$ particle with high uniformity and conformality. The Cr$_2$O$_3$ layer is amorphous and has a thickness of ~5 nm. The EDX analysis of different particle regions and XPS depth profiles analysis confirm the TiO$_2$-Cr$_2$O$_3$ core-shell structure.
**Fig. S28.** TEM image of Cr$_2$O$_3$-coated GaN nanowire with Pt cocatalyst.
Fig. S29. XPS of (a) Cr 2p and (b) Pt 4f of Pt/Cr$_2$O$_3$/GaN/n$^+$–p Si sample. The Cr 2p$_{3/2}$ binding energy at 576.9 eV and Cr 2p$_{1/2}$ binding energy at 586.8 eV are assigned to Cr$^{III}$ state from Cr$_2$O$_3$,
 and Pt 4f$_{7/2}$ binding energy at 71.3 eV and Pt 4f$_{5/2}$ binding energy at 74.5 eV correspond to metallic Pt (Pt$^0$).
**Fig. S30.** ABPE of Pt/GaN/n⁺−p Si and Pt/Cr₂O₃/GaN/n⁺−p Si samples under AM 1.5G one-sun illumination. The maximum ABPE of Pt/Cr₂O₃/GaN/n⁺−p Si is 11.8%, which is higher than that of Pt/GaN/n⁺−p Si (10.4%).
Fig. S31. Faradaic efficiency measurement of H₂ for Pt/Cr₂O₃/GaN/n⁺−p Si photocathode at 0 V vs RHE. The calculated H₂ is the theoretical amount of H₂ produced assuming 100% Faraday efficiency.
Fig. S32. J-V curves of Pt/Cr\textsubscript{2}O\textsubscript{3}/GaN/n\textsuperscript{+}\textendash p Si samples with different Cr\textsubscript{2}O\textsubscript{3} thicknesses under AM 1.5G one-sun illumination. The thickness of Cr\textsubscript{2}O\textsubscript{3} was controlled by varying the Cr(NO\textsubscript{3})\textsubscript{3} precursor concentration. It was found that a thin Cr\textsubscript{2}O\textsubscript{3} layer below 2 nm improve the PEC performance. Whereas increasing the Cr\textsubscript{2}O\textsubscript{3} layer thickness beyond 2 nm resulted in diminished photocurrent, which can be ascribed to the large tunneling resistance to electron transport associated with a thick Cr\textsubscript{2}O\textsubscript{3} layer.
**Fig. S33.** TEM image of GaN nanowire with Pt cocatalyst. Compared to Pt/Cr$_2$O$_3$/GaN/n$^+$–p Si sample (Fig. S28, ESI†), the TEM image of Pt/GaN/n$^+$–p Si shows sparser distribution of Pt nanoparticles on nanowires. ICP-AES analysis indicates the loading amounts of Pt in Pt/GaN/n$^+$–p Si and Pt/Cr$_2$O$_3$/GaN/n$^+$–p Si samples were 4.6 and 6.8 nmol cm$^{-2}$, respectively.
Fig. S34. Maximum ABPE of Pt/GaN/n\textsuperscript{+}–p Si samples as a function of Pt loading amount. By using 10, 15 and 20 \(\mu\)L of 0.2 M H\textsubscript{2}PtCl\textsubscript{6} as precursors for the photodeposition, the loading amounts of Pt in Pt/GaN/n\textsuperscript{+}–p Si samples were determined by ICP-AES analysis to be 3.1, 4.6 and 6 nmol cm\(^{-2}\), respectively. The loading amount of 6 nmol cm\(^{-2}\) Pt in Pt/GaN/n\textsuperscript{+}–p Si is comparable with that in Pt/Cr\textsubscript{2}O\textsubscript{3}/GaN/n\textsuperscript{+}–p Si (6.8 nmol cm\(^{-2}\)), whereas the maximum ABPE of Pt/GaN/n\textsuperscript{+}–p Si is 10.7\%, which is lower than that of Pt/Cr\textsubscript{2}O\textsubscript{3}/GaN/n\textsuperscript{+}–p Si (11.8\%). This indicates that the increase of Pt loading amount contributes partially to the enhanced PEC performance.
**Table S1.** Performance comparison between the presented Pt/Cr$_2$O$_3$/GaN/n$^+$-p Si photocathode and previously reported homojunction p-n Si-based photocathodes with ABPE >8% under AM 1.5G one-sun illumination.$^{[a]}$

<table>
<thead>
<tr>
<th>Photocathode</th>
<th>Onset potential (V vs RHE)</th>
<th>Current density at 0 V vs RHE (mA cm$^{-2}$)</th>
<th>ABPE (%)</th>
<th>Ref</th>
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<tr>
<td>Pt/Al$_2$O$_3$/n$^+$-p Si</td>
<td>+0.52</td>
<td>30</td>
<td>8.7</td>
<td>11</td>
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<tr>
<td>Pt/SiO$_2$/n$^+$-p Si</td>
<td>+0.49</td>
<td>30</td>
<td>8.9</td>
<td>12</td>
</tr>
<tr>
<td>Pt/n$^+$-p Si</td>
<td>+0.56</td>
<td>28</td>
<td>9.6</td>
<td>13</td>
</tr>
<tr>
<td>Pt/n$^+$-p micropyramid Si</td>
<td>+0.53</td>
<td>36</td>
<td>10</td>
<td>14</td>
</tr>
<tr>
<td>Ni–Mo/NiSi/n$^+$-p microwire Si</td>
<td>+0.55</td>
<td>30</td>
<td>10.1</td>
<td>15</td>
</tr>
<tr>
<td>Pt/GaN/n$^+$-p Si</td>
<td>+0.5</td>
<td>38</td>
<td>10.5</td>
<td>16</td>
</tr>
<tr>
<td>TiO$_2$/Pt/n$^+$-p Si</td>
<td>+0.56</td>
<td>35</td>
<td>10.8</td>
<td>17</td>
</tr>
<tr>
<td>Ni–Mo/n$^+$-p microwire Si</td>
<td>+0.5</td>
<td>36</td>
<td>10.8</td>
<td>18</td>
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<tr>
<td>IrO$_x$/TiO$_2$/F:SnO$_2$/Ti/n$^+$-p Si</td>
<td>+0.56</td>
<td>39</td>
<td>10.9</td>
<td>19</td>
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<tr>
<td>TiO$_2$/Pt/n$^+$np$^+$ Si</td>
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<td>35</td>
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<tr>
<td>Pt/Cr$_2$O$_3$/GaN/n$^+$-p Si</td>
<td>+0.52</td>
<td>39</td>
<td>11.8</td>
<td>This work</td>
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</table>

$^{[a]}$ The highest ABPE reported for Si-based photocathodes is 13.26%,$^{21}$ which was achieved by a Si heterojunction structure consisting of amorphous Si (a-Si) layer on crystalline Si (c-Si) and thus not included in the Table. The record efficiency is largely attributed to the inherent high onset potential of +0.64 V vs RHE, which is much higher than that of common homojunction p-n Si-based photocathodes ($\leq +0.56$ V vs RHE).
Reference:


