Supporting Information

Electrocatalytic Oxygen and Hydrogen Evolutions at Ni$_3$B/Fe$_2$O$_3$ Nanotube Arrays under Visible Light Radiation

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Figure S1. Nyquist plots and simulated curves of Ni$_3$B/Fe$_2$O$_3$ NTAs in dark and under one-sun radiation. The equivalent circuit is shown with the solution resistance denoted as $R_s$, the charge transfer resistor as $R_{ct}$ and the constant-phase element as CPE.

Figure S2. OER polarization curves of Ni$_3$B/Fe$_2$O$_3$ NTAs and NiOOH/Fe$_2$O$_3$ NTAs under one-sun radiation.

Figure S3. OER (a) polarization curves and (b) chronoamperograms at 1.23 V at the bare Fe$_2$O$_3$ NTAs and Fe$_2$O$_3$ NTAs modified with Ni$_3$B using different deposition times (5, 10, 20, and 30 min) under repeated on-off radiation sequences. (c) The onset potential plotted vs. deposition time.

Figure S4. IPCE and APCE spectra at 1.23 V of bare Fe$_2$O$_3$ NTAs and Fe$_2$O$_3$ NTAs modified with Ni$_3$B using different deposition times (5, 10, 20, and 30 min).
Figure S5. Field emission-SEM images of the top (a) and cross section (b) of Fe$_2$O$_3$ NTAs.

In Figure S5, the Fe$_2$O$_3$ NTAs have an average inner diameter of 55 nm and a length of 2.05 μm. The vertically oriented and aligned NTAs promote the directional charge transport due to the one-dimensionality of the tubes.$^1$

Figure S6a is a field emission-SEM image of the cross section of a Ni$_3$B/Fe$_2$O$_3$ NTA, revealing that the nanotubes have an average thickness of 2.25 μm. The thickness of the Ni$_3$B layer was determined to be around 0.20 μm from the SEM and EDS elemental mapping analysis (Figure S6b-e).

Figure S7. SEM images of Ni$_3$B/Fe$_2$O$_3$ NTAs before (a) and after OER (b) and HER (c).
A field emission-SEM image of a Ni$_3$B/Fe$_2$O$_3$ NTAs (Figure S7a) shows that the entire surface of the Fe foil was uniformly covered with Fe$_2$O$_3$ NTAs. After OER, the surface of the Ni$_3$B/Fe$_2$O$_3$ NTAs became rougher and contained numerous nanoparticles (Figure S7b). A closer examination reveals that the nanoparticles are 40 ± 10 nm in diameter. Such a morphological change is likely originated from the Ni$_3$B oxidation. After HER in alkaline solution, some small burr-like structures covered the Ni$_3$B/Fe$_2$O$_3$ NTAs (Figure S7c).

**Table S1.** Calculated values of the solution resistor ($R_s$), charge transfer resistor ($R_{ct}$) and constant phase element (CPE) on the fitted equivalent circuit of Ni$_3$B/Fe$_2$O$_3$ NTAs in dark and under one-sun radiation.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE (mF/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Under irradiation</td>
<td>1.33</td>
<td>8.44</td>
<td>34.93</td>
</tr>
<tr>
<td>In dark</td>
<td>1.36</td>
<td>13.17</td>
<td>33.56</td>
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</tbody>
</table>

**Table S2.** Best fitted parameters of time-resolved photoluminescence.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Decay lifetimes (ns)</th>
<th>Fractional contribution</th>
<th>Average lifetimes ($\tau_{\text{Avg.}}$, ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$ NTAs</td>
<td>7.50 55.54 1.33</td>
<td>0.14 0.04 0.82</td>
<td>4.36</td>
</tr>
<tr>
<td>Ni$_3$B/Fe$_2$O$_3$ NTAs</td>
<td>7.79 48.05 1.55</td>
<td>0.14 0.04 0.82</td>
<td>4.28</td>
</tr>
</tbody>
</table>

**Reference**