Supporting Information

Surface treatment with Al\(^{3+}\) on Ti-doped \(\alpha\)-Fe\(_2\)O\(_3\) nanorod arrays photoanode for efficient photoelectrochemical water splitting

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**Fig. S1** XPS survey spectra of Fe\(_2\)O\(_3\)-Al and Ti-Fe\(_2\)O\(_3\)-Al.
The onset potential of dark current can provide information as to electrocatalytic activity of water oxidation on the Fe$\textsubscript{2}$O$\textsubscript{3}$ electrode.\textsuperscript{1} Compared with Fe$\textsubscript{2}$O$\textsubscript{3}$ and Ti-Fe$\textsubscript{2}$O$\textsubscript{3}$, the dark onset potential of Fe$\textsubscript{2}$O$\textsubscript{3}$-Al and Ti-Fe$\textsubscript{2}$O$\textsubscript{3}$-Al shows an anodic shift. In general, a lower dark current onset potential indicates higher electrocatalytic activity for water oxidation.\textsuperscript{2} This indicates that the surface treatment with Al$^{3+}$ makes the electrode less catalytic for O$_2$ evolution.

The donor concentration ($N_d$) and flat band potential ($V_{fb}$) can be quantified by the Mott-Schottky equation.\textsuperscript{3}

$$\frac{1}{C^2} = \frac{2}{en_e\varepsilon_N} \left( \frac{V}{V_{fb}} - kT/e \right)$$

Where the $C$ is the capacitance of the space charge region, $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ is the dielectric constant of $\alpha$-Fe$_2$O$_3$, $e$ is the electron charge, $V$ is the electrode applied potential, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $N_d$ is the donor concentration. In general, the impact of temperature term is small and can be neglected. All samples show a positive slope in the Mott-Schottky plots, indicating that they are n-type semiconductors. The donor concentration is calculated with the equation.\textsuperscript{4, 5}

$$N_d = \left( \frac{2}{ne\varepsilon_0} \right) \left[ \frac{d(1/C^2)}{dV} \right]^{-1}$$

With the $\varepsilon$ value of 80 for $\alpha$-Fe$_2$O$_3$, the $N_d$ of Fe$_2$O$_3$ and Fe$_2$O$_3$-Al were calculated to be $2.1\times10^{18}$ cm$^{-3}$. The $N_d$ of Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$-Al were calculated to be $1.7\times10^{20}$ cm$^{-3}$. 

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**Fig. S2** Dark current for water oxidation (a) and Mott-Schottky plots (b) of Fe$_2$O$_3$, Fe$_2$O$_3$-Al, Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$-Al.
As shown in the Fig. S3, the dark current of Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$-Al are negligible with N$_2$ bubbling. When O$_2$ was bubbling into the solution, an obvious reduction current was observed for Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$-Al. The reduction current represents the electrons of Fe$_2$O$_3$ reduce O$_2$. Compared with Ti-Fe$_2$O$_3$, the Ti-Fe$_2$O$_3$-Al has a higher reduction current when O$_2$ was bubbling into solution. The same result can be seen on Fe$_2$O$_3$ and Fe$_2$O$_3$-Al. When O$_2$ was bubbling into the solution, Fe$_2$O$_3$-Al has a higher reduction current than Fe$_2$O$_3$. The results suggest that O$_2$ is reduced more easily on Fe$_2$O$_3$-Al and Ti-Fe$_2$O$_3$-Al compared with Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$.

References