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Supporting Information

Surface treatment with Al^{3+}on Ti-doped α-Fe_2O_3 nanorod arrays photoanode for efficient photoelectrochemical water splitting

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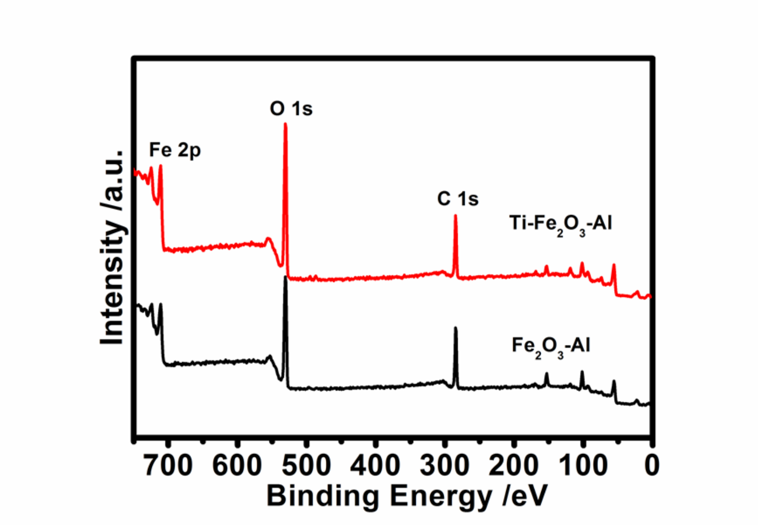

Fig. S1 XPS survey spectra of Fe_2O_3-Al and Ti-Fe_2O_3-Al.

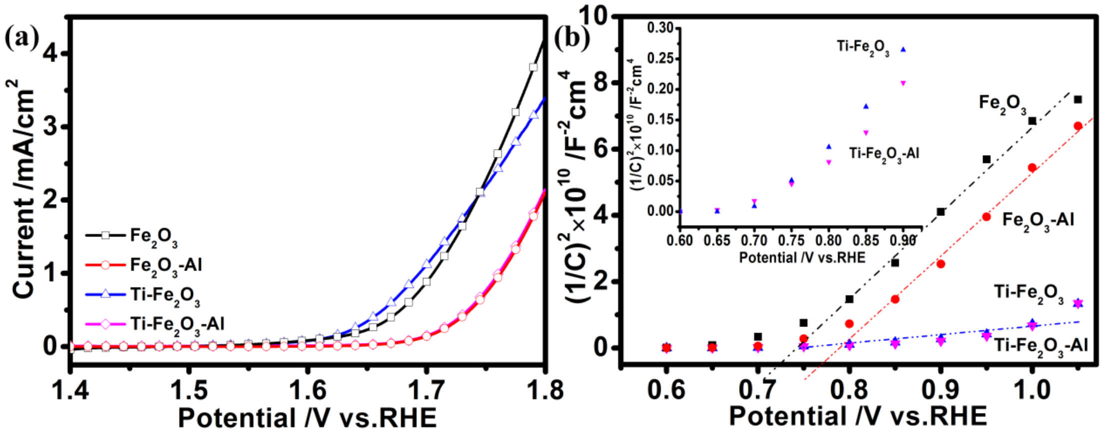

Fig. S2 Dark current for water oxidation (a) and Mott-Schottly plots (b) of Fe_2O_3, Fe_2O_3-Al, Ti-Fe_2O_3 and Ti-Fe_2O_3-Al.

The onset potential of dark current can provide information as to electrocatalytic activity of water oxidation on the Fe_2O_3 electrode.[1] Compared with Fe_2O_3 and Ti-Fe_2O_3, the dark onset potential of Fe_2O_3-Al and Ti-Fe_2O_3-Al shows an anodic shift. In general, a lower dark current onset potential indicates higher electrocatalytic activity for water oxidation.[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.[3]

$$1/C^2 = (2/e\varepsilon_0\varepsilon N_d)[(V - V_{fb}) - kT/e]$$

Where the C is the capacitance of the space charge region, ε_0 is the vacuum permittivity, ε is the dielectric constant of α-Fe_2O_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.[4, 5]

$$N_d = (2/e\varepsilon\varepsilon_0)[d(1/C^2)/dV]^{-1}$$

With the ε value of 80 for α-Fe_2O_3,[6] the N_d of Fe_2O_3 and Fe_2O_3-Al were calculated to be 2.1×10^{18} cm^{-3}. The N_d of Ti-Fe_2O_3 and Ti-Fe_2O_3-Al were calculated to be 1.7×10^{20}cm^{-3}.

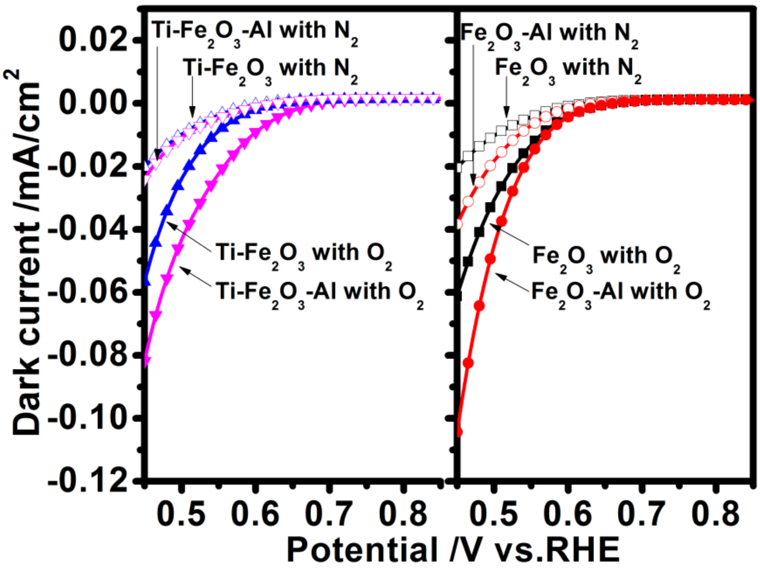

Fig. S3 Reduction dark current curves of Fe_2O_3, Fe_2O_3-Al, Ti-Fe_2O_3 and Ti-Fe_2O_3-Al, in 1 M NaOH solution with different gas bubbling (N_2 or O_2).

As shown in the Fig. S3, the dark current of Ti-Fe_2O_3 and Ti-Fe_2O_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_2O_3 and Ti-Fe_2O_3-Al. The reduction current represents the electrons of Fe_2O_3 reduce O_2. Compared with Ti-Fe_2O_3, the Ti-Fe_2O_3-Al has a higher reduction current when O_2 was bubbling into solution. The same result can be seen on Fe_2O_3 and Fe_2O_3-Al. When O_2 was bubbling into the solution, Fe_2O_3-Al has a higher reduction current than Fe_2O_3. The results suggest that O_2 is reduced more easily on Fe_2O_3-Al and Ti-Fe_2O_3-Al compared with Fe_2O_3 and Ti-Fe_2O_3.

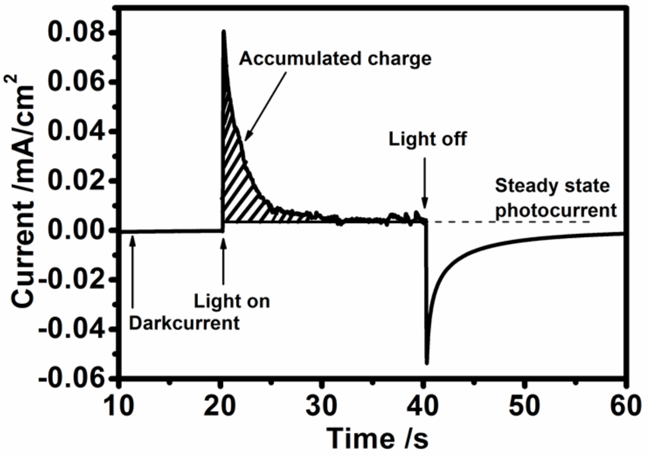

Fig. S4 The transient photocurrent of Fe_2O_3 at 1.5 V_{RHE}. 1 M NaOH, 100 mW/cm^2.

References

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