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Electronic Supplementary Information

Tuning the ion permeability of Al_2O_3 coating layer on Fe_2O_3 photoanode for improved photoelectrochemical water oxidation

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Figure S1. XRD patterns for Ti-Fe₂O₃ (black), Ti-Fe₂O₃/CBD-Al₂O₃ (red), and Ti-Fe₂O₃/ALD-Al₂O₃ (blue). The substrate is FTO glass.

Since the substrate is FTO glass, the peaks at $26.5^{\circ} 38.9^{\circ}$, 51.6° are obviously identified for the SnO₂ (JCPDS 77-0450). And the peaks at 35.6° , 64.1° are assigned to lattice plane (110) and (300) for Fe₂O₃ (JCPDS 87-1166), respectively. No signal of Al₂O₃ was observed because the thickness of Al₂O₃ overlayer loaded through CBD or ALD is only several nano meters (< 5 nm).



Figure S2 XPS spectrum of Ti 2p for as-prepared Ti-Fe₂O₃.

As shown in **Fig. S2**, the XPS spectrum for Ti 2p was observed for as-prepared Ti-Fe₂O₃. The binding energy for $2p_{3/2}$ and $2p_{1/2}$ is 458.0 eV and 463.7 eV, respectively. Comparing to those of pure TiO₂ (458.5 eV for $2p_{3/2}$ and 464.3 eV for $2p_{1/2}$), the slight decrease of binding energy confirms the doping of Ti ions into Fe₂O₃ lattices. And the doping concentration of Ti is ~ 0.4 at%.



Figure S3 UV-Vis transmittance spectra for Ti-Fe₂O₃ (black), Ti-Fe₂O₃/CBD-Al₂O₃ (red), and Ti-Fe₂O₃/ALD-Al₂O₃ (blue).



Figure S4. CV plots of Ti-Fe₂O₃ (a), Ti-Fe₂O₃/CBD-Al₂O₃ (b), and Ti-Fe₂O₃/ALD-Al₂O₃ (c) were obtained at different scan rates from 10 to 320 mV s⁻¹ in the dark. The current for any sample is only attributed to capacitive charging in the sweep potential range from 0.8 V to 1.2 V, in which no redox reaction occurs in the dark condition.



Figure S5. Mott-Schottky plots of Ti-Fe₂O₃ (black), Ti-Fe₂O₃/CBD-Al₂O₃ (red), and Ti-Fe₂O₃/ALD-Al₂O₃ (blue).

The values of $1/C^2$ were directly obtained by the workstation (Princeton Applied Research, 2273), then the capacitance as a function of potential was transformed into C-V plots shown in Fig. 5b. According to pervious report, the surface capacitance of semiconductor electrodes would be affected significantly by the oxides overlayer. And the Mott-Schottky analysis can be applied for the characterization of the passive film-electrolyte interface.³ Therefore we utilize this method to evaluate the capacitance of CBD-Al₂O₃ and ALD-Al₂O₃.



Figure S6 FT-IR spectrum of Ti-Fe₂O₃ treated with CBD process without annealing

As shown in Fig. S6, the wavenumber of 1074.2 cm^{-1} is assigned to Al-OH bending.⁴ Meanwhile, the peaks at 3469.7, 3365.7 cm⁻¹ might be attributed to Al-OH stretching.⁵ The 1342.4 cm⁻¹ corresponding to C=O ⁶ is identified to the urea used in the CBD bath, which will be removed during the annealing treatment. The H-O-H bending exhibits the peak of 1628.1 cm⁻¹, indicating the absorption of water.⁷



Figure S7 O 1s spectrum of Ti-Fe₂O₃ treated by CBD process without annealing

Fig. S7 displays XPS spectrum of O 1s for Ti-Fe₂O₃ treated by the chemical bath process without annealing. As previous report,⁸ the peaks at 532.3, 531.8 and 530.3 eV are responsible to absorbed water, hydroxide group and Al-O-Al, respectively. The

main part of O 1s is attributed to hydroxide, indicating that aluminum hydroxide was formed after the CBD process without annealing treatment.



Figure S8 Open circuit potential (OCP) measurements of Ti-Fe₂O₃, Ti-Fe₂O₃/CBD-Al₂O₃, and Ti-Fe₂O₃/ALD-Al₂O₃ photoanodes under irradiation of 300 W Xe lamp.



Figure S9. a)The J-V curves(J_{H_2O}) in 1 M NaOH, b) J-V curves ($J_{Na_2SO_3}$)in 1 M NaOH with 0.5 M Na₂SO₃, c)Bulk charge separation efficiency (ϕ_{sep}) for Ti-Fe₂O₃ (black), Ti-Fe₂O₃/CBD-Al₂O₃ (red), and Ti-Fe₂O₃/ALD-Al₂O₃ (blue).



Figure S10. The equivalent circuits of photoanodes: a) Ti-Fe₂O₃, b) Ti-Fe₂O₃/CBD-Al₂O₃ and Ti-Fe₂O₃/ALD-Al₂O₃.

As shown in Fig. 6d, the Nyquist plots for Ti-Fe₂O₃/CBD-Al₂O₃ (red), and Ti-Fe₂O₃/ALD-Al₂O₃ (blue) were measured at 1.23 V in 1M NaOH under AM1.5G illumination, while the frequency varied from 100 kHz to 0. 1 Hz. Obviously, the Nyquist plots of all samples exhibited the similar EIS behaviors at the low and high frequency. Since the charge carriers in the semicondutor and ions in the electrolyte response to different frequency during EIS measurement, the high-frequency region is considered to reflect the bulk property of Ti-Fe₂O₃ substrate for all pthotoandoes. And the low-frequency part of Nyquist plots is assigned to the interface between electrodes and electrolyte.⁹ Hence, the EIS behavior in low-frequency region was paid more attention to analyze charge transfer at the photoanode-electrolyte interface for Φ_{inj} .

According to EIS behavior, the equivalent circuits for Ti-Fe₂O₃ and Ti-Fe₂O₃/ALD-Al₂O₃, and Ti-Fe₂O₃/CBD-Al₂O₃ were drawn in Fig. S10a and S10b. The proposed models consist of the following circuit components. The R_s represents the resistance of potential control circuit. It is expressed by the intercept of the Nyquist plot at high frequency. The parallel connection of R_{bulk} and C_{bulk} denoted the resistance and capacitance of the Ti-Fe₂O₃ for all photoanodes, corresponding to the high-frequency part. And Csc/E is utilized to describe the interface capacitance between semiconductor electrode and electrolyte. Meanwhile, R_{et,SC/E} is the charge transfer resistance at the semiconductor-electrolyte interface, which is associated with the reaction rate of OER. As the uniform coating of CBD-Al₂O₃ and ALD-Al₂O₃ prevented the Ti-Fe₂O₃ from being exposed to the electrolyte, the C_{bulk} of Ti-Fe₂O₃/CBD-Al₂O₃ or ALD-Al₂O₃ only connects with R_{bulk} in parallel. In contrary, bare Ti-Fe₂O₃ contacts with electrolyte, which results in the parallel connection between the C_{bulk} of Ti-Fe₂O₃ and the interface components donated as R_{ct,SC/E}C_{SC/E}, where the R_{ct,SC/E}C_{SC/E} means the parallel connection of R_{ct,SC/E} and C_{SC/E}.

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