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Supporting Information

Stoichiometric water splitting using a *p*-type Fe₂O₃-based photocathode with the aid of a multi-heterojunction

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Figure S1. Raman spectra for N,Zn-Fe₂O₃ (red line) and pristine-Fe₂O₃ (blue line) electrode.



Figure S2. HAXPES VB spectra for N_2 (red line) and pristine-Fe₂O₃ (blue line) electrode. The binding energy means the energy difference between VB and the Fermi level.



Figure S3. Mott–Schottky plot of N,Zn-Fe₂O₃ electrode measured in 0.5 M Na₂CO₃–NaHCO₃ (1:1) buffer electrolyte (pH 9.7) under dark at 10 Hz. The negative slope indicates that N,Zn-Fe₂O₃ is a *p*-type semiconductor. The flat band potential of VB can be estimated from the potential of the intersection point between the plot and x-axis. The perturbation around 1.3 V is presumably due to defect states or surface states located above the valence band maximum.



Figure S4. Cubic roots of photoelectric quantum yield as a function of incident photon energies from photoelectron spectroscopy measurements in air for N,Zn-Fe₂O₃ (red circles) and Cr_2O_3 (blue circles) on glass after immersion in 0.5 M NaHCO₃-Na₂CO₃ (1:1) buffer solution. The ionic potential of these materials were determined from the energy of the intersection point between the background line and the extrapolation of the cubic roots of photoelectron emission yield.



Figure S5 UV/Visible absorption spectra for N,Zn-Fe₂O₃ before (black dashed line) and after the 1 h stability test with irradiation of AM1.5 (1 sun, 100 mW cm⁻²) at +0.1 V vs. RHE in a mixed aqueous solution of 0.5 M Na₂CO₃-NaHCO₃ (1:1) (green line), and at +0.04 V vs. RHE in 0.2 M K₂SO₄ (red line).



Figure S6. Photoelectrochemical property measured in 0.2 M K₂SO₄ electrolyte (pH 5.9). (a) Current-potential characteristics and (b) photocurrent transients at +0.1 V vs. RHE under 1 sun (100 mW cm⁻², AM 1.5) illumination for bare N,Zn-Fe₂O₃ (gray line), Pt/TiO₂/N,Zn-Fe₂O₃ (blue line), and Pt/TiO₂/N,Zn-Fe₂O₃ (red line). (c) Current–potential characteristics for the bare N,Zn-Fe₂O₃ before (gray line) and after (orange line) the 1 h PEC stability test at +0.1 V vs. RHE, and of the as-prepared Pt/N,Zn-Fe₂O₃ electrode (green line)



Figure S7. The background-subtracted Fe 2*p* hard X-ray photoelectron spectroscopy (HAXPES) spectra (dot) and fitting curves (solid line; total of 3 components, dashed line; each component after deconvolution) for the deactivated N,Zn-Fe₂O₃ electrode monitored at detecting angles of 3° (red) and 54° (blue). The background was subtracted by Shirley method. The fitting was conducted by using 3 components Voigt function. The component 1, 2 and 3 were mainly attributed to Fe²⁺, Fe³⁺ and satellite, respectively.³⁸ The error bars show the 95% confidential interval ($\pm 1.96 \times$ standard deviation from the fitted curve). The difference of the peak between data monitored at 3° and 54° was larger than confidential intervals, which indicated that the difference in the deactivated N,Zn-Fe₂O₃ electrode is statistically significant.



Figure S8. Cross-sectional of (a) TEM and (b) high-resolution TEM images for Pt nanoparticle on N,ZnFe₂O₃.



Figure S9. XRD patterns for TiO₂ on a glass substrate. The sample was prepared under the same conditions as those for the photocathode; sputtering for TiO₂ under Ar/O₂ (4:1 v/v) on glass, followed by annealing at 823 K under N₂/O₂ (4:1 v/v) gas flow. Triangle and square markers indicate the diffraction peaks from anatase (101) (PDF#00-021-1272) and rutile (110) (PDF#00-021-1276), respectively.



Figure S10. UV/visible absorption spectra for N,Zn-Fe₂O₃ (black line), TiO₂/N,Zn-Fe₂O₃ (green line), TiO₂/N,Zn-Fe₂O₃/Cr₂O₃ (red line), TiO₂ (blue line), and Cr₂O₃ (orange line) on TCO coated glass, and *n*-SrTiO_{3-x} (gray dotted line). The thickness of the N,Zn-Fe₂O₃, TiO₂, and Cr₂O₃ layers are 190, 10, and 10 nm, respectively.



Figure S11. Current-potential characteristics under chopped visible light ($\lambda > 420$ nm) irradiation for Pt/TiO₂/N,Zn-Fe₂O₃ (blue line), and Pt/TiO₂/N,Zn-Fe₂O₃ (red line). The light from solar simulator was irradiated through the long-pass filter (SCF-42L, Sigma-Koki).



Figure S12. XRD patterns for Cr_2O_3 on a Si substrate. The sample was prepared under the same conditions as those for the photocathode; sputtering of Cr on the Si substrate followed by annealing at 823 K under N_2/O_2 (4:1 v/v) gas flow for 2 h. Arrow markers indicate the diffraction peaks from α -Cr₂O₃ (PDF#00-006-050).



Figure S13. Current-potential characteristics for Pt/TiO₂/pristine-Fe₂O₃/Cr₂O₃ measured in 0.5 M Na₂CO₃–NaHCO₃ (1:1) buffer electrolyte (pH 9.7) under 1 sun (AM 1.5, 100 mW cm⁻²) illumination. The electrode was prepared by the same procedure with Pt/TiO₂/N,Zn-Fe₂O₃/Cr₂O₃ except for N and Zn doping. A negligibly small cathodic photocurrent was observed in this control experiment, which indicated that the diffused Cr into Fe₂O₃ did not act as a dopant to enhance cathodic photocurrent in Pt/TiO₂/N,Zn-Fe₂O₃/Cr₂O₃.



Figure S14. Cross-sectional of large-scale TEM image for (a) $Pt/TiO_2/N_2nFe_2O_3$ and (b) $Pt/TiO_2/N_2nFe_2O_3/Cr_2O_3$.



Figure S15. Current–potential characteristics for Cr_2O_3 measured in a mixed solution of 0.5 M NaHCO₃-Na₂CO₃ (1:1). Chopped light (300 W Xe lamp, light intensity: c.a. 50 Sun) was illuminated onto a quartz cell containing the 10 nm Cr_2O_3 thick layer on the TCO electrode. The results indicate that the Cr_2O_3 has *p*-type conductivity. However, this photocurrent of Cr_2O_3 cannot contribute to the enhanced photocurrent of Pt/TiO₂/N,Zn-Fe₂O₃/Cr₂O₃, because 99.9% of the irradiated light at shorter than 400 nm is absorbed by the TiO₂ and N,Zn-Fe₂O₃ layers in front of Cr_2O_3 .



Figure S16. Absolute value of current density-voltage (|J|-V) curves for the *n*-SrTiO_{3-x} photoanode (red line) and Pt/TiO₂/N₂Zn-Fe₂O₃/Cr₂O₃ photocathode (green line) in 0.5 M NaHCO₃-Na₂CO₃ (1:1) buffer solution under chopped simulated solar illumination (100 mW cm⁻², AM 1.5). |J|-V curves for the photocathode as measured in the tandem cell position (simulated solar illumination filtered by the *n*-SrTiO_{3-x} photoanode) are shown as the blue line.



Figure S17. Photocurrent transients for a two-electrode tandem system of $Pt/TiO_2/N$,Zn-Fe₂O₃/Cr₂O₃ and SrTiO_{3-x} under 1 sun (AM1.5) irradiation with no external electrical bias. The light was irradiated to both $Pt/TiO_2/N$,Zn-Fe₂O₃/Cr₂O₃ and SrTiO_{3-x} from the SrTiO_{3-x} side (red line) or irradiated only onto SrTiO_{3-x} (blue line). A two-electrode system consisting of Pt wire and SrTiO_{3-x} was also evaluated as a control experiment (green line). The reactions were carried out in an aqueous solution of 0.5 M Na₂CO₃-NaHCO₃ (1:1).