**Supporting Information**

**Cathodic shift in onset potential of solar oxygen evolution on hematite by 13-group oxide overlayers**

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## Experimental Details

Semitransparent hematite thin films were prepared as photoanodes according to the previously described method.[1] Fluorine-doped tin oxide (FTO) substrates (TEC 15, Hartford Glass Co.) were modified with a monolayer of $SiO_x$ by spraying TEOS (99.999%, Aldrich) 10 vol.% in ethanol. Then, 20 mL of an ethanol solution of 10 mM iron(III) acetylacetonate ($Fe(acac)_3$, 97%, Aldrich) was sprayed on the substrates placed on a hotplate at 793 K. The thickness of typical hematite thin films was estimated to be 27–30 nm based on the absorbance (46% and 22%) and the reported absorption coefficients ($(44 \text{ nm})^{-1}$ and $(118 \text{ nm})^{-1}$) at 400 and 550 nm, respectively.[2,3] Thinner hematite thin films were prepared by reducing the amount of the sprayed solution to investigate effect of the film thickness. For comparison, hematite thin films doped with $Ga^{3+}$ (approximately 1.0–7.5 mol% with respect to $Fe^{3+}$) were prepared by spraying a 10 mM $Fe(acac)_3$ ethanol solution containing appropriate amounts of $Ga(NO_3)_3 \cdot nH_2O$ (99.9%, Alfa Aesar).

The hematite thin films were modified with $Al_2O_3$, $Ga_2O_3$, or $In_2O_3$ overlayers by facile CBD methods. The hematite thin films were immersed into 100 mL of water at approximately 348 K. To this solution, 0.938 g of $Al(NO_3)_3 \cdot 9H_2O$ (99%, Fluka) and 15.2 g of urea (99.5%, Fluka); 0.418 g of $Ga(NO_3)_3 \cdot nH_2O$ and 6.01 g of urea; or 0.409 g of $In(NO_3)_3 \cdot nH_2O$ (In >29%, Alfa Aesar) and 6.01 g of urea were added successively with an interval of a few minutes under mild stirring. After 10–15 minutes of the urea addition, the thin films were rinsed with water and calcined at 773 K for 2 h in a typical case. X-ray photoelectron spectroscopy (XPS) was performed by Axis Ultra (Kratos analytical) with a monochromatic Al Ka X-ray source (1486.6 eV) to confirm the presence of the overlayer. As shown in Figure S5 and Table 1, signals of $Fe_2O_3$ were significantly reduced or absent after the deposition of the overlayer. Therefore, the thicknesses of the as-deposited overlayers were comparable to or thicker than an escape depth of photoelectrons (a few nanometers).

A $Ga_2O_3$ overlayer, which was promising in particular, was further characterized before and after photoelectrochemical (PEC) water splitting with a scanning electron microscope (FEI, XLF30-FEG). Facets of a FTO substrate 30–300 nm in dimension were observed after the deposition of $Ga_2O_3$ (Figure S4b), suggesting that a $Ga_2O_3$ overlayer the thickness of which was a couple tens of nanometers at most was deposited conformally on hematite in the early stage of the CBD process. Note that $Ga(OH)_3$ precipitated in a bath solution when the CBD process was extended. Such precipitates could attach on the surface of a hematite photoanodes and remain as aggregates. After PEC water splitting for approximately one hour, XPS signals of $Fe_2O_3$ were observed (Figure S5d), indicating that excessive overlayer was etched in a strong alkaline medium. Indeed, the surface of a $Ga_2O_3$-deposited hematite photoanode became rougher slightly and nanoparticles smaller than 40 nm appeared on the surface, which were presumably attributable to $Ga_2O_3$. These $Ga_2O_3$ nanoparticles

could release lattice strain of a hematite thin film and passivate surface traps. However, they were not likely to work as active sites for water oxidation because photoexcited holes would not migrate to such large nanoparticles.

The photoanodes before and after the CBD treatment were modified with $Co^{2+}$ ions according to the previously reported method.[4,5] This treatment is supposed to form a $Co^{2+}$ monolayer on hematite surface which catalyzes water oxidation via hole trapping by Co-centers.[4] The photoanodes were immersed into an aqueous solution of 10 mM $Co(NO_3)_2 \cdot 4H_2O$ (98%, Alfa Aesar) for a few seconds and then rinsed with distilled water. Likewise, the hematite thin films were modified with $Ga^{3+}$ ions using a 10 mM $Ga(NO_3)_3$ aqueous solution. Photocurrent measurements were performed in a three-electrode configuration using 1 M NaOH aqueous solution (pH 13.6) as an electrolyte solution, a Pt wire as a counter electrode, and an Ag/AgCl electrode in saturated KCl solution as a reference electrode. The light source was simulated sunlight from a 450 W xenon lamp (Osram, ozone free) through a KG3 filter (3 mm, Schott) with a measured intensity equivalent to standard AM1.5 sunlight (100 mW $cm^{-2}$, spectrally corrected) at the sample face. The irradiation area on the hematite was limited to 0.5 $cm^{-2}$ with a mask. To obtain *J-V* curves, the potential of the hematite photoanodes was swept at a scan rate of 50 mV $s^{-1}$ from cathodic to anodic potentials with and without the irradiation unless otherwise noted. The potential was converted to the RHE potential.[2] Photocurrent was defined by difference of anodic currents with and without the irradiation to cancel contribution of dark reactions and electric double layers that was dependent on the actual area immersed to the electrolyte. Transient photocurrent responses were measured by chopping the incident light frequency at 0.5 Hz and scanning the potential at 5 mV $s^{-1}$ and recorded every 0.5 mV. Chronoamperometry was carried out by irradiating the photoanodes with the simulated sunlight. After irradiation for three hours at 1.0 V vs. RHE, the potential was switched between 1.0 and 1.2 V vs. RHE every 15 minutes. IPCE measurements were performed under irradiation of a 300 W xenon lamp with integrated parabolic reflector (Cermax PE 300 BUV) passing through a monochromator (Bausch & Lomb, bandwidth 10 nm FWHM). The number of photons was measured with a Si photodiode.

For analysis of gaseous product under irradiation, a constant-volume system made of borosilicate glass was connected to a vacuum pump and a gas chromatograph (HRGC 5300, Carlo Erba). MS-5A columns (60/80 mesh, length: 5 m, diameter: 3.1 mm, Restek), He carrier gas (99.999%, Carba gas) and a TCD detector (HWD 430, Carlo Erba) were employed for gas separation and detection. After evacuation, the system was filled with 100 mbar of He. The potential of the working electrode was controlled at +1.08 V to a Pt counter electrode in a two-electrode configuration. After a reaction for one hour in dark, a $Ga_2O_3$-modified hematite photoanode with an

active area of 4 cm$^2$ was irradiated with a 150 W halogen lamp (Osram, HLX 64640,) through a KG3 filter. The temperature of the solution was kept at 290 K by flowing cooling water during the reaction. $N_2$ as much as 60 μmol was detected in 30 h due to imperfect evacuation and leakage of air. To eliminate contribution of the air, one-fourth of the amount of $N_2$ was subtracted from that of $O_2$.

The total transmittance and total reflectance spectra were measured with a Varian Cary 5 spectrophotometer equipped with an 11 cm diameter integrating sphere coated with polytetrafluoroethylene (PTFE).[1] Absorption spectra were calculated with the formula, $A = 1 - T - R$, where $A$, $T$, $R$ were absorption, total transmittance, and total reflectance, respectively. Hematite photoanodes were wetted with water and covered with a quartz window to duplicate the conditions during the PEC water splitting.

## References

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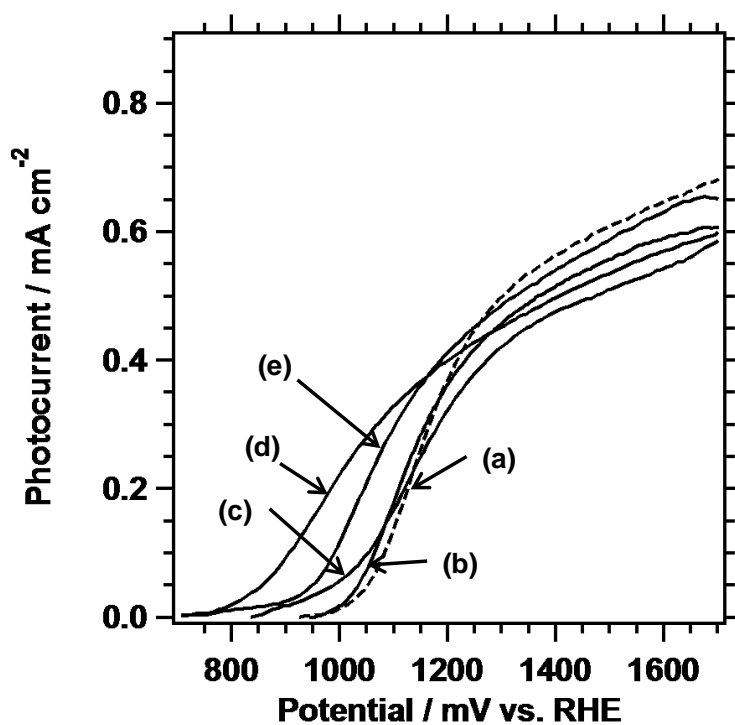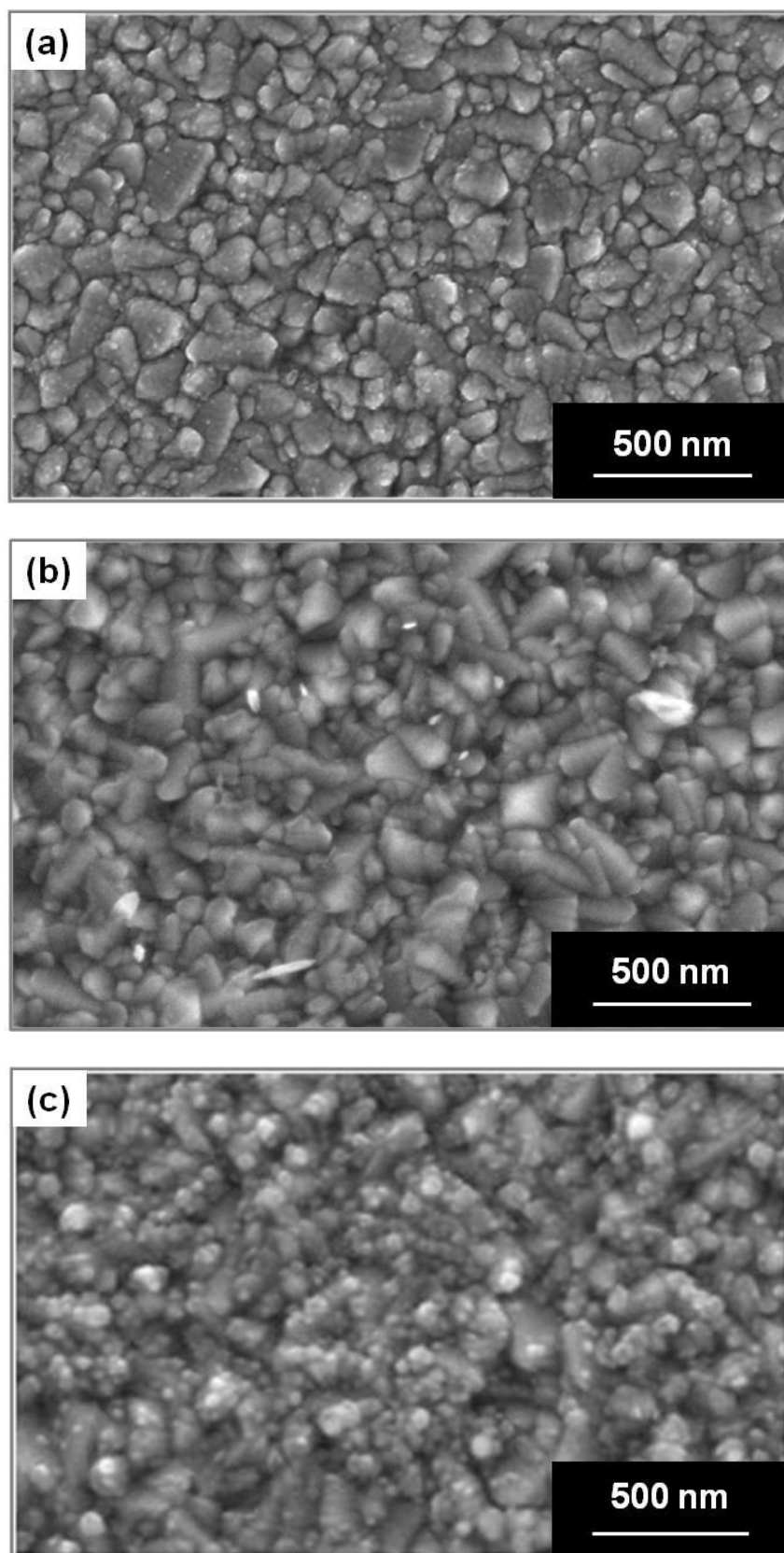
**Figure S1.** Photocurrent-potential curves of (a) bare hematite (dashed line), (b) annealed hematite, and hematite photoanodes modified with (c) $Al_2O_3$, (d) $Ga_2O_3$, and (e) $In_2O_3$ by CBD. Annealing temperature: 773 K.
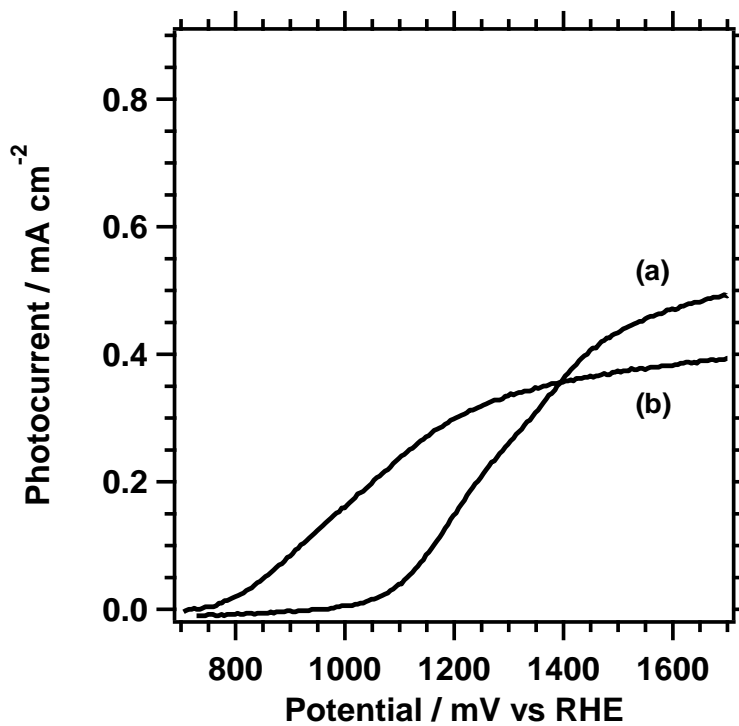


**Figure S2.** Photocurrent-potential curves of hematite photoanodes prepared by spraying 10 mL of the $Fe(acac)_3$ ethanol solution. (a) Bare and (b) $Ga_2O_3$-deposited hematite photoanodes.
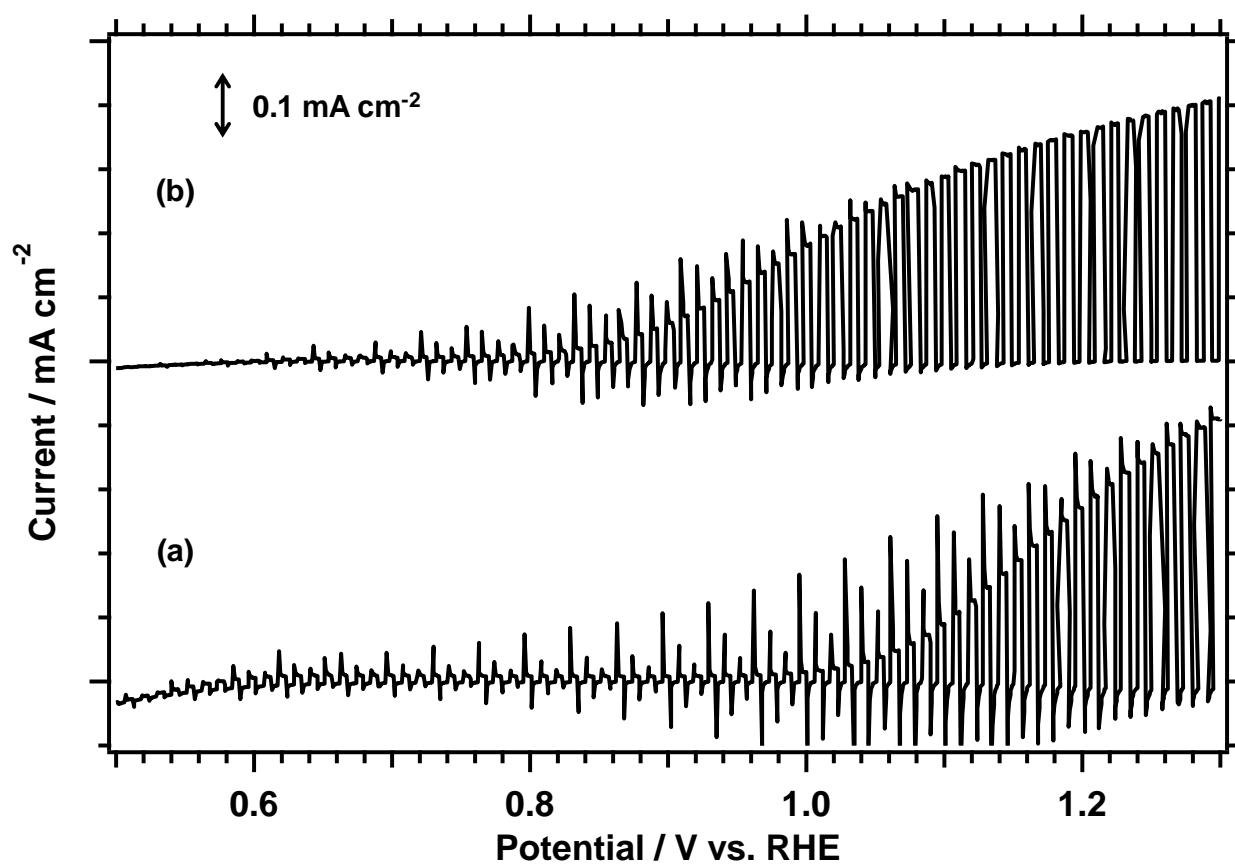
**Figure S3.** Current-potential curves of (a) as-made and (b) $Ga_2O_3$-deposited hematite photoanodes under chopped light irradiation. The potential was scanned to the anodic side at 5 mV s$^{-1}$.

**Figure S4.** SEM images of hematite photoanodes. (a) An unmodified sample, (b) a sample modified

with a $Ga_2O_3$ overlayer, and (c) (b) after PEC water splitting.
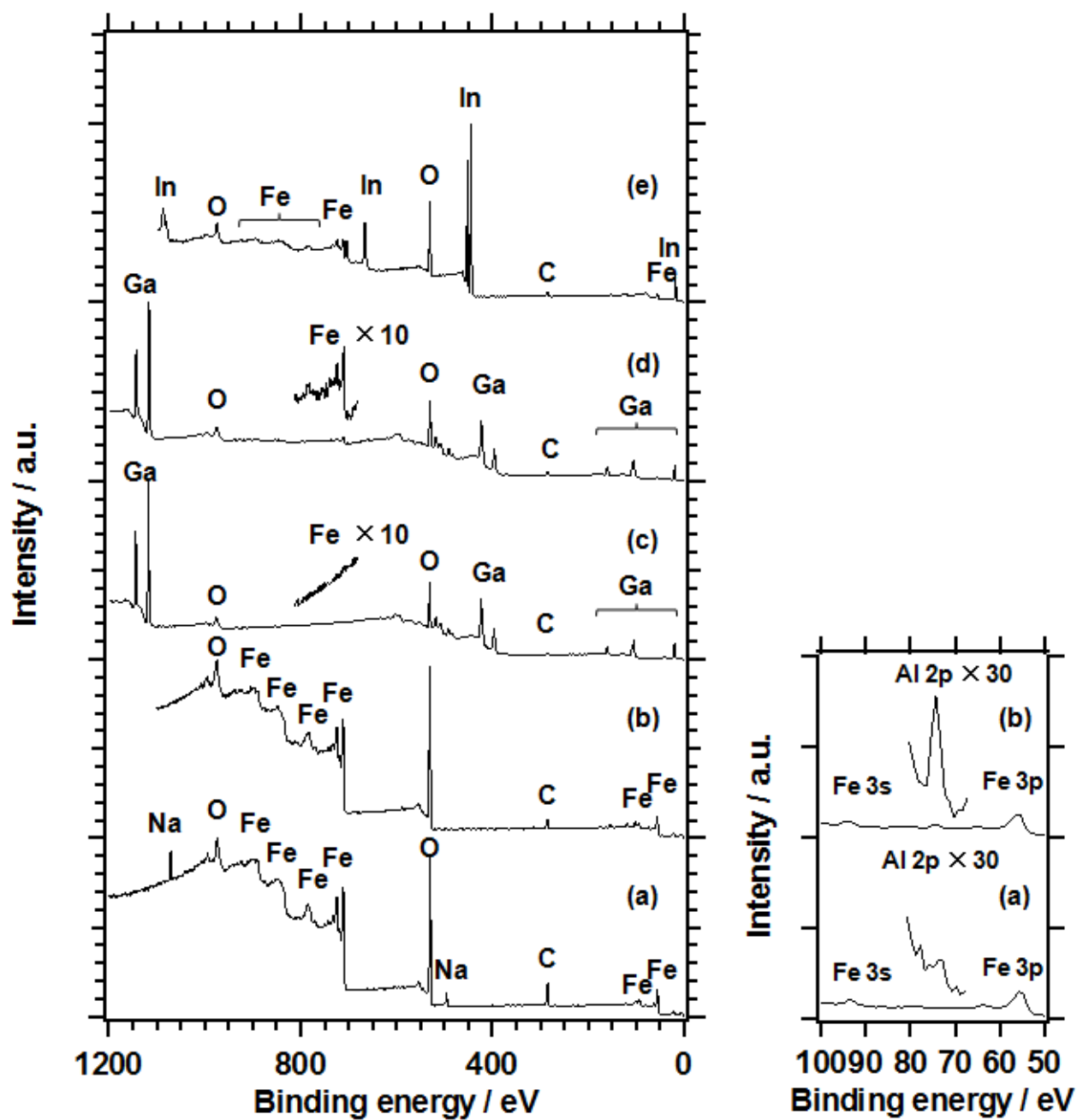
**Figure S5.** XPS spectra of hematite photoanodes (a) unmodified and (b–e) modified with an overlayer. Overlayers: (b) $Al_2O_3$, (c) $Ga_2O_3$, (d) $Ga_2O_3$ after PEC water splitting, and (e) $In_2O_3$. Peaks of Na in spectrum (a) were attributed to the residual electrolyte (NaOH).
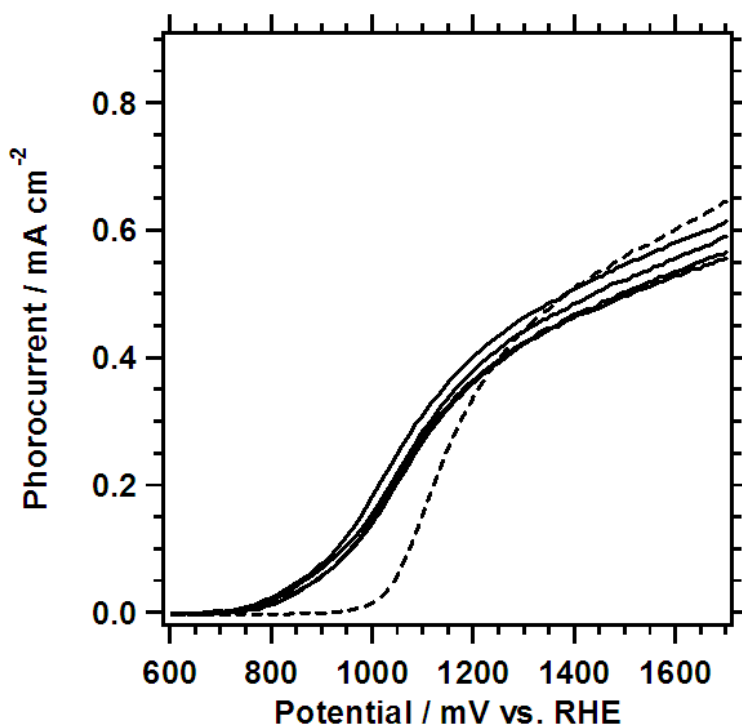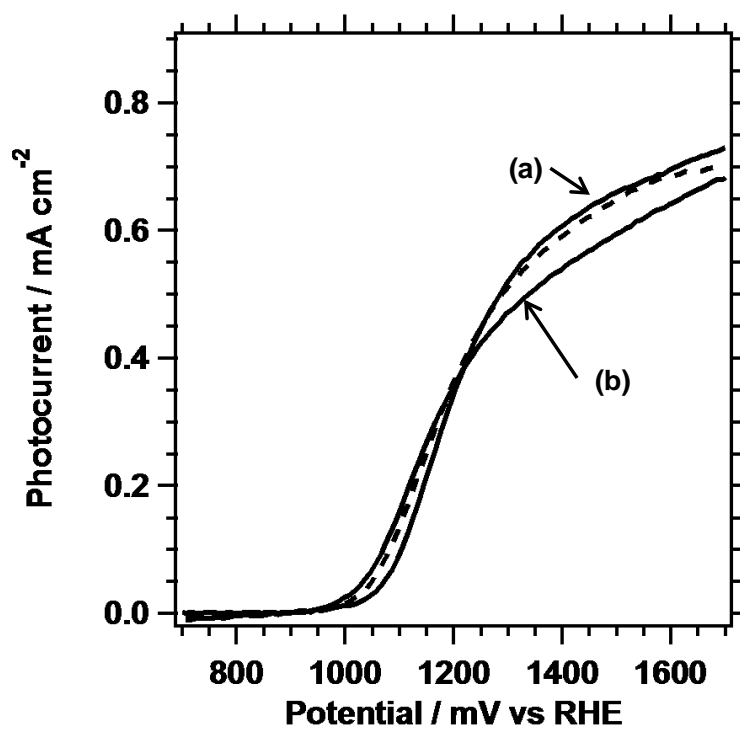
**Figure. S6.** Photocurrent-potential curves of a bare hematite (dashed line) and hematite photoanodes modified with $Ga_2O_3$ in a bath solution for 15–60 min (solid lines). Samples were annealed at 773 K for 2 hours.
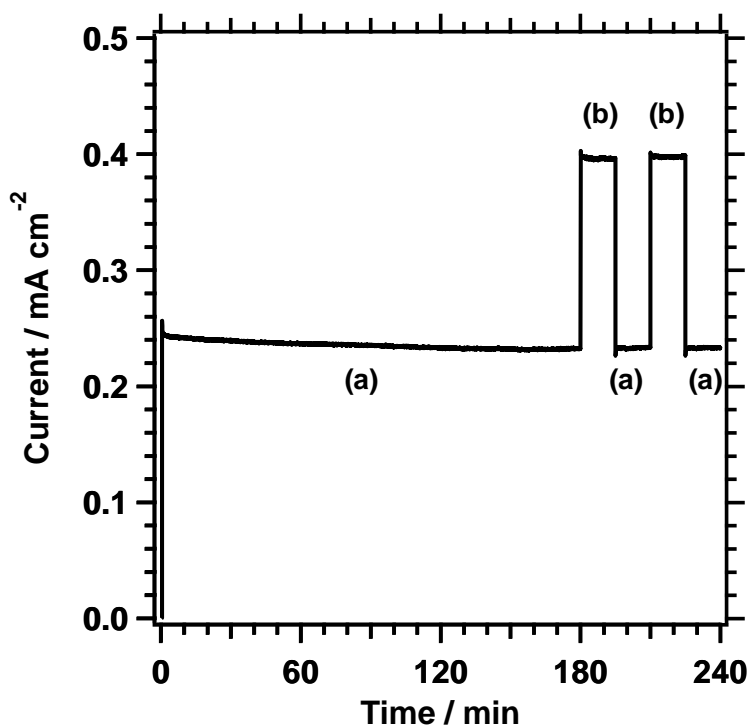
**Figure. S7.** Chronoamperometry of a hematite photoelectrode coated with $Ga_2O_3$ by the CBD method at an applied potential of (a) +1.0 V and (b) + 1.2 V vs. RHE.

**Figure S8.** Photocurrent-potential curves of hematite photoanodes (a) immersed in a 10 mM Ga(NO$_3$)$_3$ aqueous solution and (b) doped with 4.5% Ga. Dashed line shows a photocurrent-potential curve of an bare hematite.