Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Photoelectrochemical water-splitting over a surface-modified p-type Cr_2O_3 photocathode

Keita Sekizawa,* Keiichiro Oh-ishi, and Takeshi Morikawa

Toyota Central R&D Laboratories, Inc., 41-1, Yokomichi, Nagakute, Aichi 480-1192 (Japan)

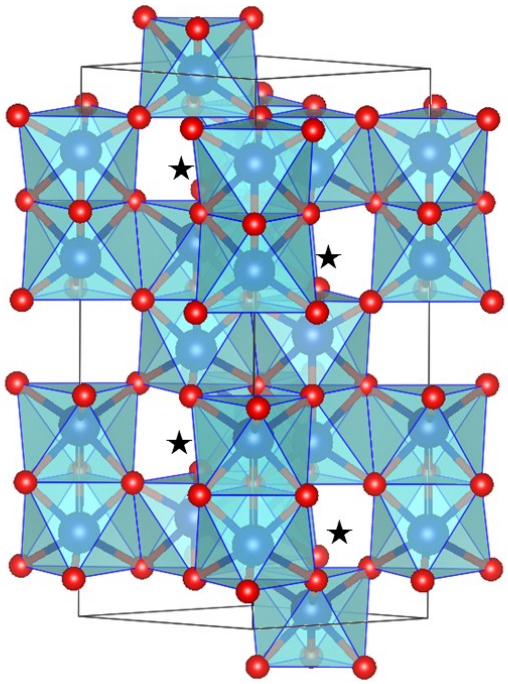

Figure S1 Structure of α-Cr_2O_3. The blue and red spheres are chromium and oxygen atoms, respectively. The light blue octahedrons are oxygen octahedral occupied by chromium. Asterisks are some examples of unoccupied octahedral sites.

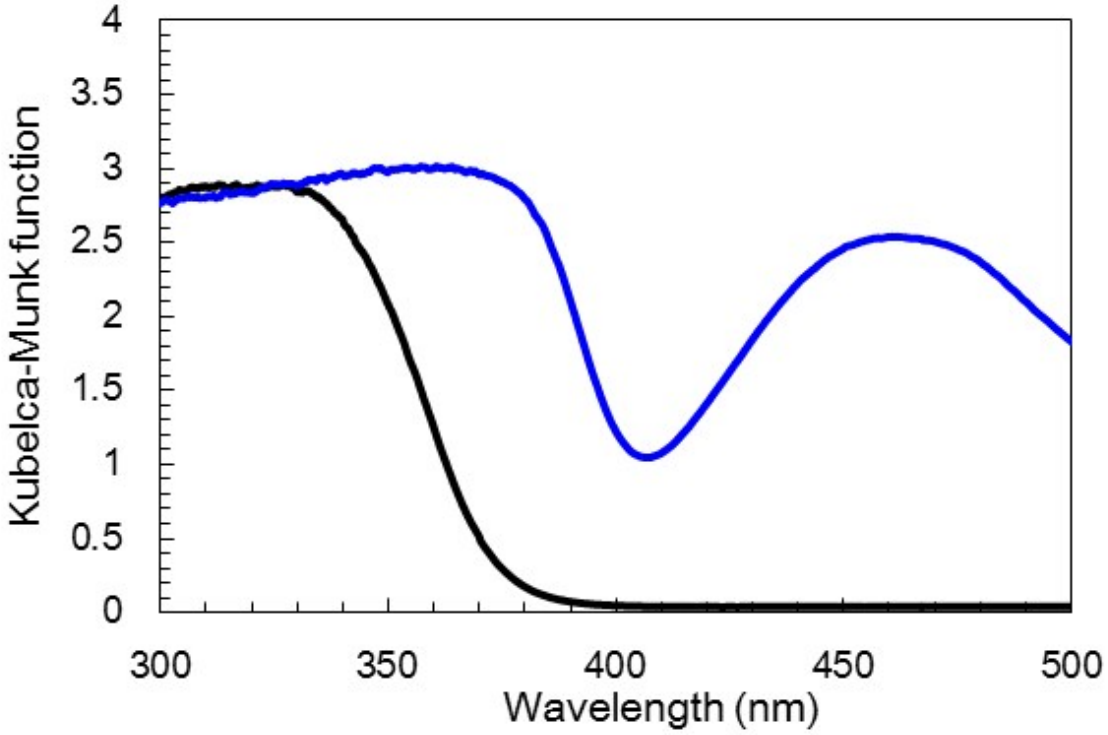

Figure S2 UV/Visible diffuse reflectance spectra of Cr_2O_3 (blue line) and TiO_2 (black line) reference bulk powders. Although Cr_2O_3 powder exhibited an absorption band with a peak at 460 nm due to high-density defects, the absorption band below 410 nm is attributed to the band-gap excitation[52-54].

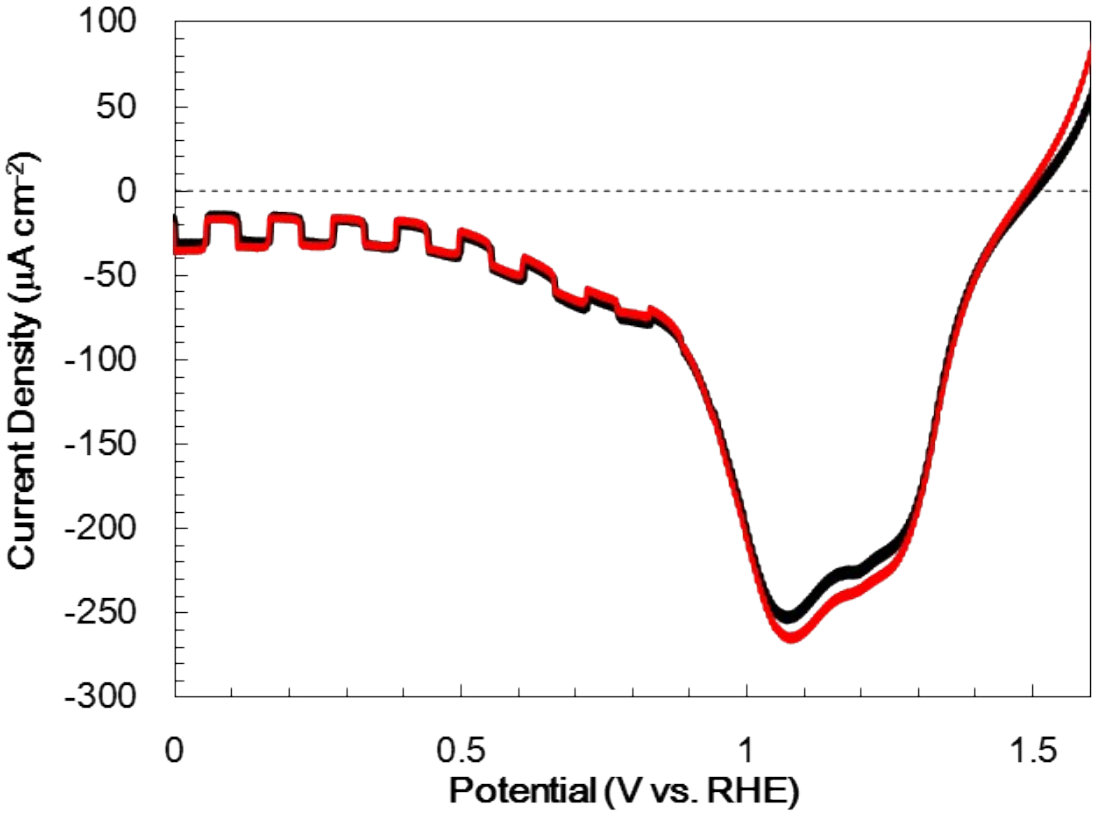

Figure S3. Photocurrent–potential characteristics for bare Cr_2O_3 before (black line) and after (red line) the 1h photoelectrolysis at +0.11 V vs. RHE in a 0.5 M Na_2CO_3–$NaHCO_3$ (1 : 1) buffer electrolyte (pH 9.7) under chopped one sun (100 mW cm^{-2}, AM 1.5) illumination.

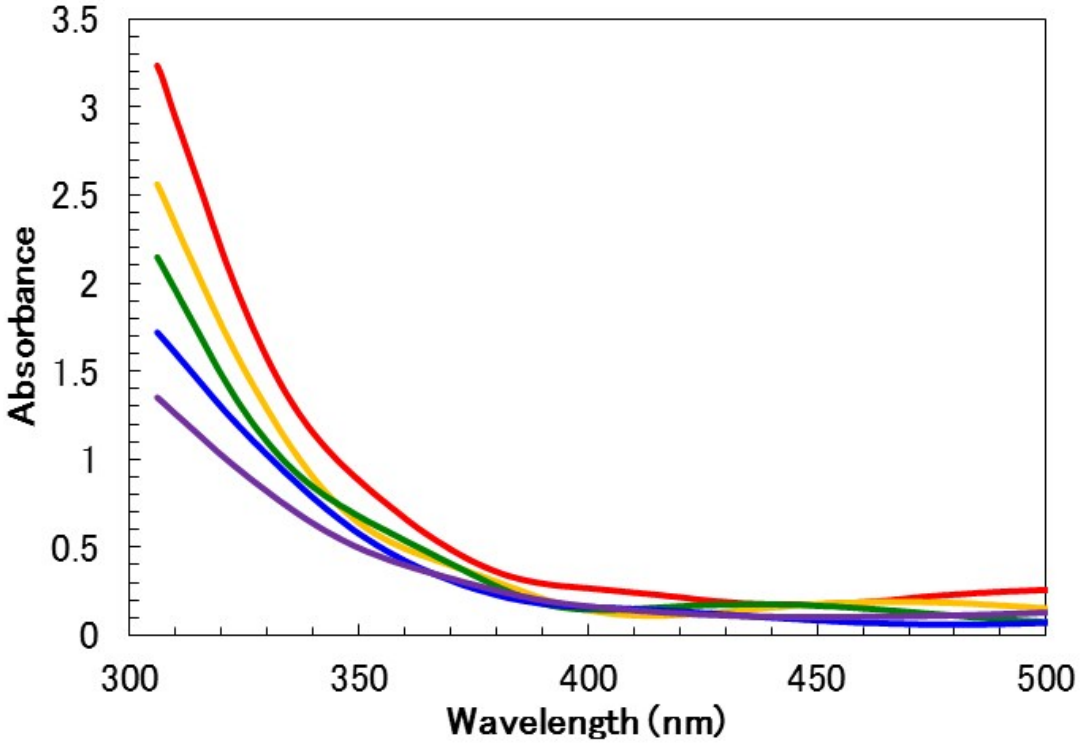

Figure S4 UV/Visible absorption spectra obtained from $Pt/TiO_2/Cr_2O_3$ electrodes at various wavelengths using different TiO_2 layer thicknesses (10 nm; purple, 30 nm; blue, 60 nm; green, 80 nm; yellow and 120 nm; red).

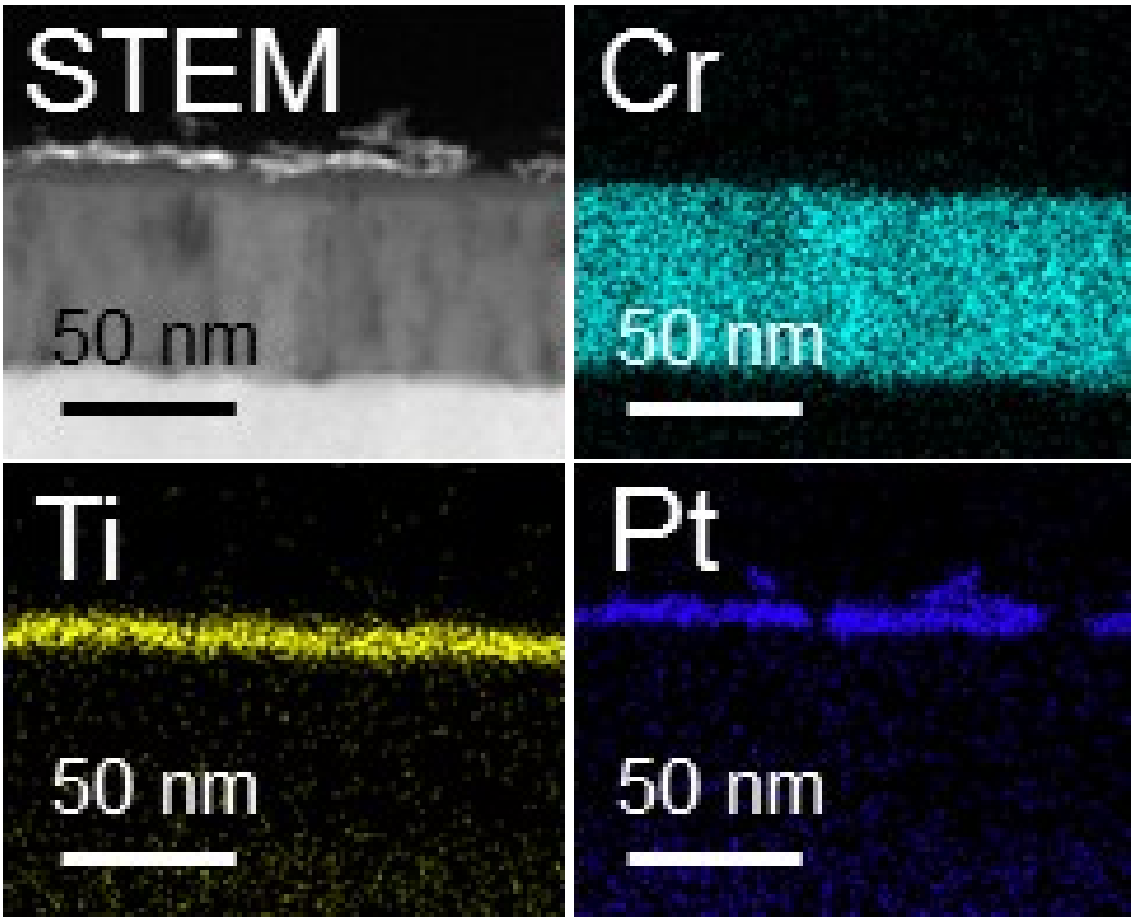

Figure S5 Cross-sectional STEM images and STEM-EDX elemental maps for Pt/TiO_2/Cr_2O_3 with 10 nm TiO_2 thickness.

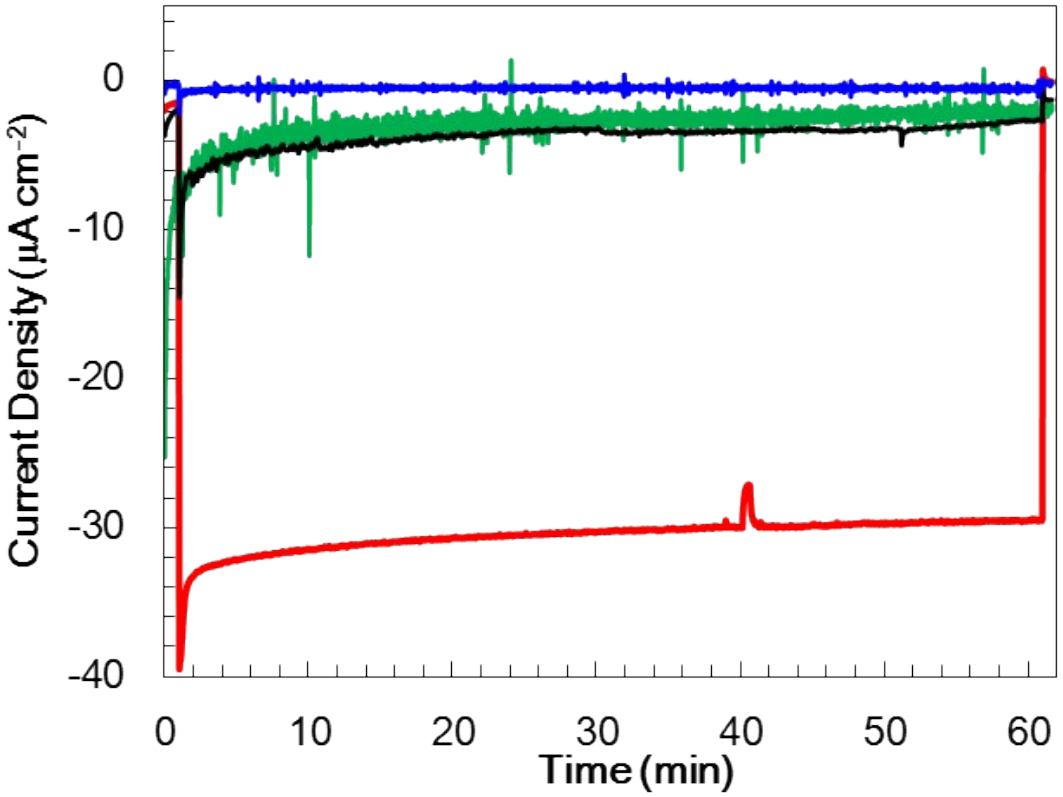

Figure S6 Time course of photocurrent for PEC water splitting under one sun (AM 1.5) irradiation with applying bias at +0.11 V vs. RHE for $Pt/TiO_2/Cr_2O_3$ (red line), bare Cr_2O_3 (black line), TiO_2/Cr_2O_3 (blue line) and Pt/Cr_2O_3 (green line). The reaction was carried out in a 0.5 M Na_2CO_3–$NaHCO_3$ (1:1) aqueous solution.