

Electronic Supplementary Information

Visible-Light-Driven Water Oxidation at a Polychromium-Oxo-Electrodeposited TiO₂ Electrode as a New Type of Earth-Abundant Photoanode

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Supporting Information

1. Experimental details.
2. Characterization of the pre-treated solution.
3. Characterization of the polychromium-oxo (Cr^{III}_xO_y)-deposited TiO₂ electrode.
4. Photocurrent responses and photoelectrocatalysis on the Cr^{III}_xO_y-deposited TiO₂ electrode.

1. Experimental details.

Materials

Titanium dioxide (TiO₂) paste (JGC Catalyst and Chemicals Ltd., PST-18NR), chromium (III) nitrate nonahydrate and all other reagents were purchased and used as received. ITO-coated glass (< 10 Ω/□ of a sheet resistance) was purchased from AGC Fabritech Co. Ltd. Deionized water was used for all the experiments.

Preparation

TiO₂ electrode

TiO₂ paste was coated on an ITO substrate (1.0 cm² area) by a baker film applicator and then air-dried for 60 min. It was calcined at 723 K for 60 min to form a TiO₂-coated ITO substrate.

Cr^{III}_xO_y-deposited TiO₂ electrode

Typically, an aqueous chromium (III) nitrate solution (0.14 mol L⁻¹, 10 mL) was pre-treated by cathodic polarization of a platinum plate electrode (2.0 cm² area) at -0.74 V vs. Ag/AgCl for 2 h. The pre-treated Cr(NO₃)₃ solution was characterized by UV-visible absorption, and Raman spectroscopic techniques (see text). A polychromium-oxo layer was cathodically electrodeposited on a TiO₂ electrode at -0.74 V vs. Ag/AgCl in the pre-treated Cr(NO₃)₃ solution for 6 h to give polychromium-oxo-deposited TiO₂ electrode. It was characterized by UV-visible absorption, XPS, Raman spectroscopic, SEM and EDS techniques.

Cr₂O₃ powder

Cr₂O₃ powder was chemically prepared as follows. An 0.3 mol L⁻¹ aqueous sodium hydroxide solution (5 mL) was slowly dropped into an 0.14 mol L⁻¹ aqueous chromium(III) nitrate solution (5 mL) to give Cr₂O₃ powder. It was repeatedly washed with water to remove sodium nitrate, and then dried at 80°C for overnight.

TiO₂ electrode with Cr₂O₃ deposited chemically

A TiO₂ electrode with Cr₂O₃ deposited chemically was prepared as follows. An 0.14 mol L⁻¹ aqueous chromium(III) nitrate solution (50 μL) followed by an 0.3 mol L⁻¹

aqueous sodium hydroxide solution (50 μL) was slowly dropped onto the TiO_2 electrode. The electrode was air-dried for several hours and then dried at 80°C for overnight to give a TiO_2 electrode with Cr_2O_3 deposited chemically.

Measurements

UV-visible absorption spectra were measured using a photodiode array spectrophotometer (Shimadzu, Multispec-1500). UV-visible diffuse reflectance spectra were measured using an UV-visible spectrophotometer (JASCO V-550) in a diffuse reflectance mode. Raman spectra were measured using a Raman spectrophotometer (Horiba, Lab RAM HR) using 532 nm excitation and silicon standard wavenumber (520.7 cm^{-1}). A scanning electron microscopic (SEM) data and energy dispersive X-ray spectroscopy (EDS) data were recorded using a scanning electron microscope (JEOL, JSM-6510LV). For analysis of the chromium amount deposited, polychromium-oxo-electrodeposited TiO_2 on the ITO electrode was dissolved in an aqua regia, and the chromium amount in the dissolved solution was measured using an inductively coupled plasma mass (ICP-MS) spectrometer (Yokogawa, HP4500). X-ray photoelectron spectroscopic (XPS) data were taken using an X-ray photoelectron spectrometer (JEOL, JPS-9000). Electrochemical experiments were conducted in a 0.1 mol L^{-1} phosphate buffer solution ($\text{Na}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4$, $\text{pH} = 7$) in an electrochemical cell equipped with a working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode using an electrochemical analyzer (Hokuto denko, HZ-3000). All the electrochemical and photoelectrochemical experiments were carried out under argon atmosphere at 298 K. A 500 W Xenon lamp (Ushio, UXL-500SX, lamp house: SX-U1500XG) with 420 nm band-pass filter or a 150 W halogen lamp (Tokina, KTS-150RSV) with a L42 UV-cut-filter ($\lambda < 420\text{ nm}$ cutoff) were used for photoelectrochemical measurements. A 500 W Xenon lamp with monochromator (Bunkoukeiki, M10) was used for incident photon-to-current efficiency (IPCE) measurement. The IPCE values were calculated according to Eq. (1),

$$\text{IPCE} = \frac{1.24 \times 10^{-6} J}{P \lambda} \quad (1)$$

where J , P and λ are a photocurrent density (A cm^{-2}), light intensity (W cm^{-2}) and wavelength (m). Initial internal quantum efficiency for oxygen evolution (Φ_{O_2}) was calculated according to Eq. (2).

$$\Phi_{O_2} = \frac{J_{\text{ini}} h c N_A}{Q P \lambda (1-T)} \quad (2)$$

where J_{ini} , h , c , N_A , Q , P , λ and T are initial current density ($42 \mu\text{A cm}^{-2}$), Plank's constant ($6.626 \times 10^{-34} \text{ J s}$), light velocity ($2.998 \times 10^8 \text{ m s}^{-1}$), Avogadro number ($6.02 \times 10^{23} \text{ mol}^{-1}$), Faradaic constant ($96,500 \text{ C mol}^{-1}$), light intensity (15.8 mW cm^{-2}), wavelength (420 nm), and transmittance (0.05). Gas evolved during the photoelectrocatalysis was analyzed on a gas chromatograph (Shimadzu, GC-8A) equipped with a molecular sieve 5\AA column using argon carrier gas (flow rate is $40 \text{ cm}^3 \text{ min}^{-1}$) at 323 K . The O_2 evolved during photoelectrocatalysis was also detected in the headspace of the gas-tight photoelectrochemical cell by an optics oxygen sensor (FOXY-21G) attached to a multifrequency phase fluorometer (NeoFox). The equipment for photoelectrochemical experiment is shown in the following photograph.



Characterization of the pre-treated solution.

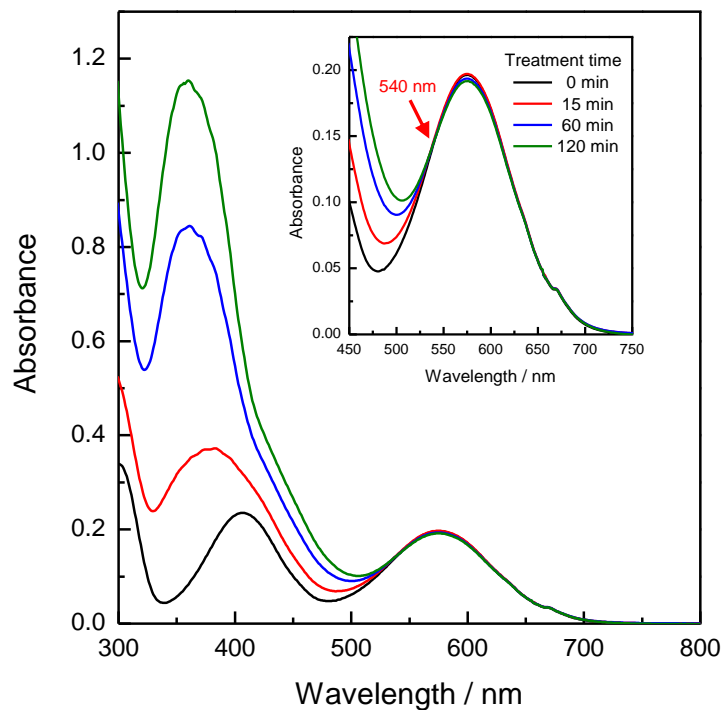


Figure S1 UV-visible absorption spectral change of a 0.14 mol L⁻¹ aqueous chromium (III) nitrate solution (10 mL) by cathodic polarization of a platinum plate at -0.74 V vs. Ag/AgCl during the pre-treatment. Two absorption bands at 410 and 580 nm are assigned to ${}^4A_{2g} \rightarrow {}^4T_{1g}$ and ${}^4T_{2g}$ d-d transition of Cr^{III} ions, respectively (*J. Catal.* 1996, **158**, 236-250.).

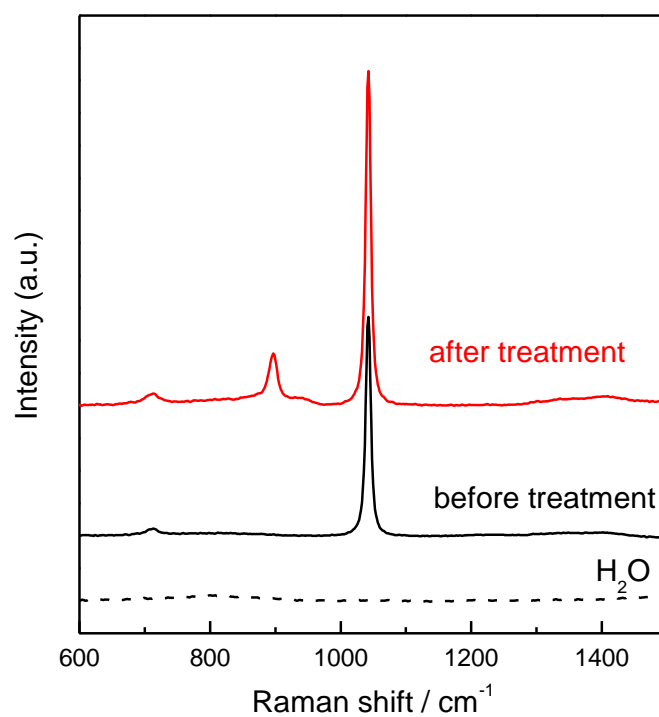


Figure S2 Raman spectra of an aqueous $\text{Cr}(\text{NO}_3)_3$ solution before (black) and after (red) the cathodic treatment (polarization of a platinum plate at -0.74 V vs. Ag/AgCl for 2 h), and blank spectrum (black dashed line) without $\text{Cr}(\text{NO}_3)_3$.

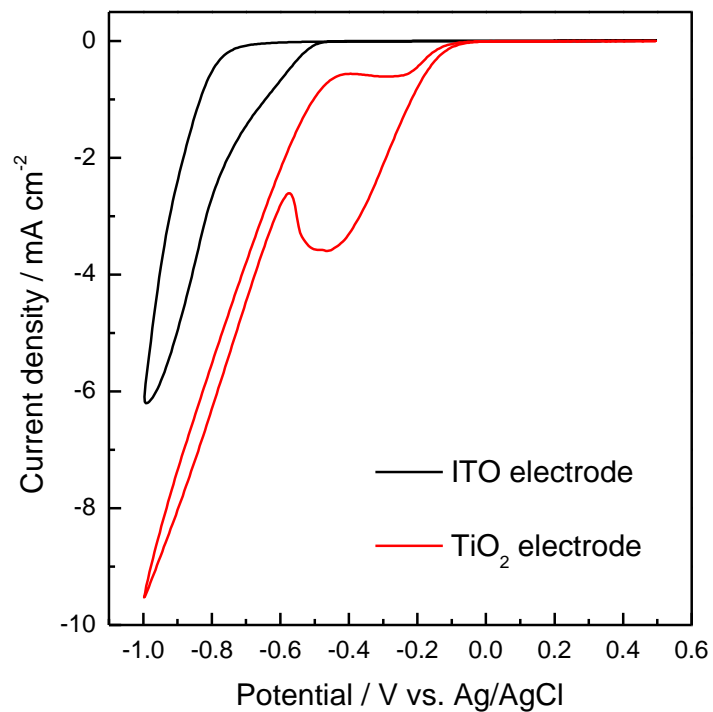


Figure S3 Cyclic voltammograms (CVs) of an ITO electrode (black) and a TiO₂ electrode (red) in the pre-treated aqueous Cr(NO₃)₃ solution (polarization of a platinum plate at -0.74 V vs. Ag/AgCl for 2 h).

2. Characterization of the $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode.

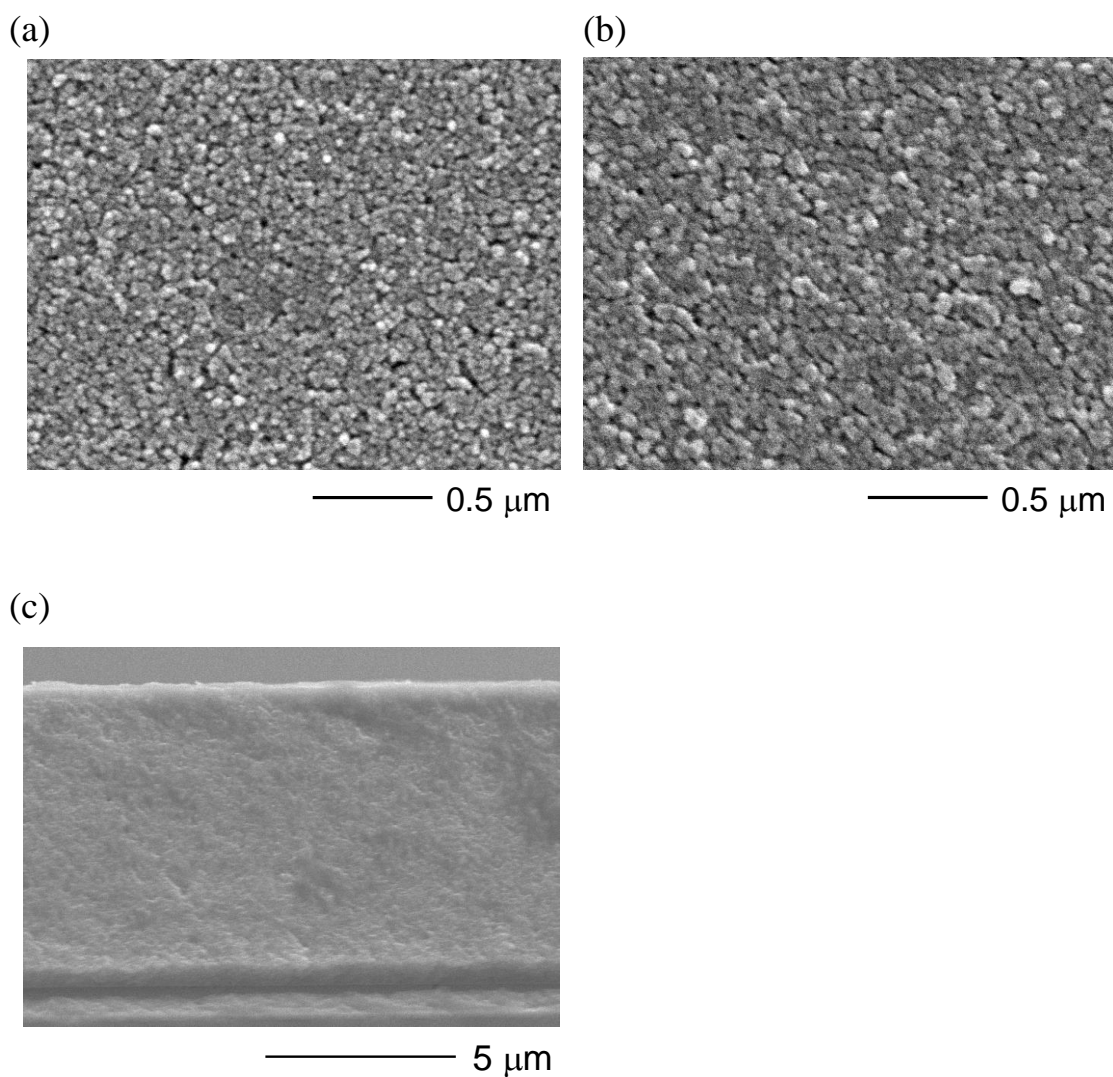


Figure S4 Scanning electron microscopic (SEM) images of (a) a neat TiO_2 electrode surface, (b) a $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode surface. (c) cross-sectional SEM image of a $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode. The film thickness (8 μm) of the $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode is nearly the same as that of the neat TiO_2 electrode for the SEM observation

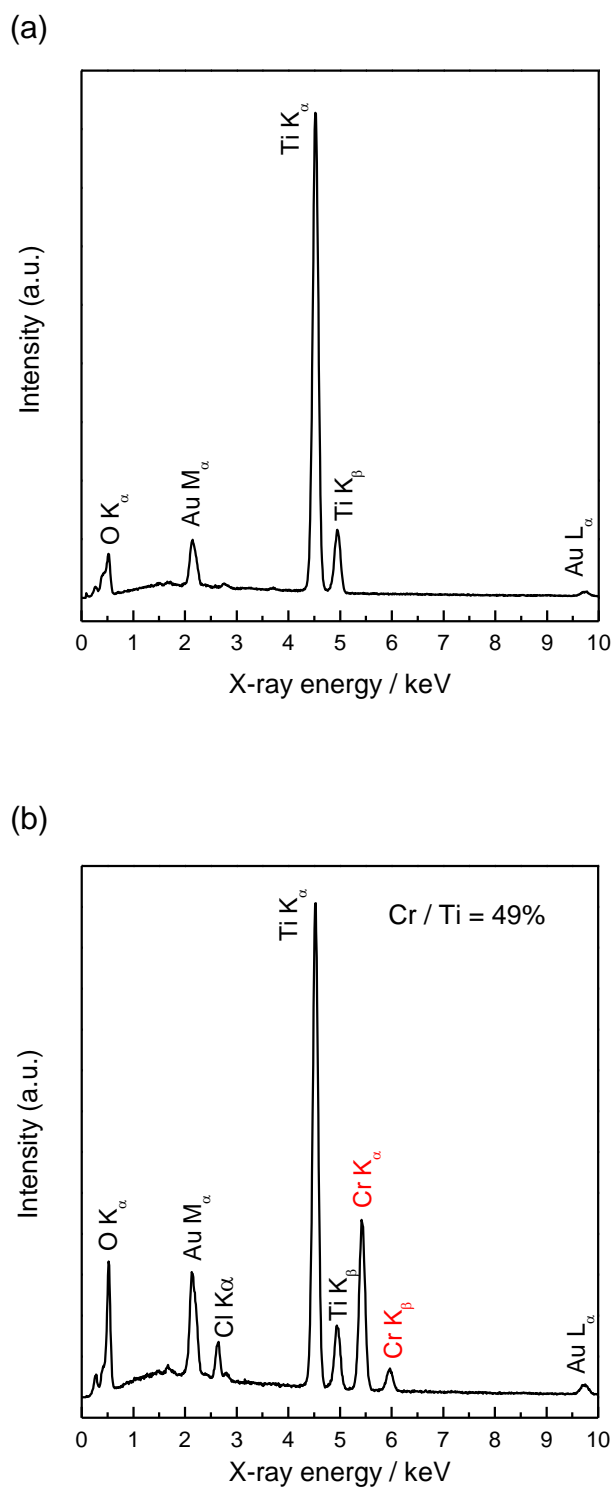


Figure S5 EDS spectra of (a) a TiO_2 electrode and (b) a $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode. The ratio in atom number of Cr / Ti on the $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode is 49%.

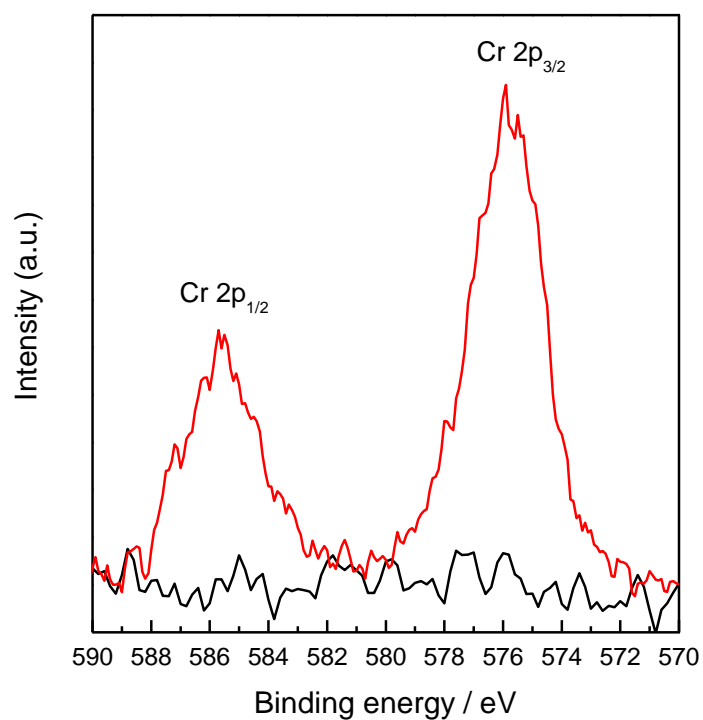


Figure S6 X-ray photoelectron spectra (XPS) of a TiO₂ electrode (black) and a Cr^{III}_xO_y-deposited TiO₂ electrode (red). It was prepared by cathodic polarization in the pre-treated aqueous Cr(NO₃)₃ solution (0.14 mol L⁻¹) at -0.74 V vs. Ag/AgCl for 6 h. The peaks at 585.7 and 575.9 eV are assigned to Cr 2p_{1/2} and Cr 2p_{3/2}, respectively.

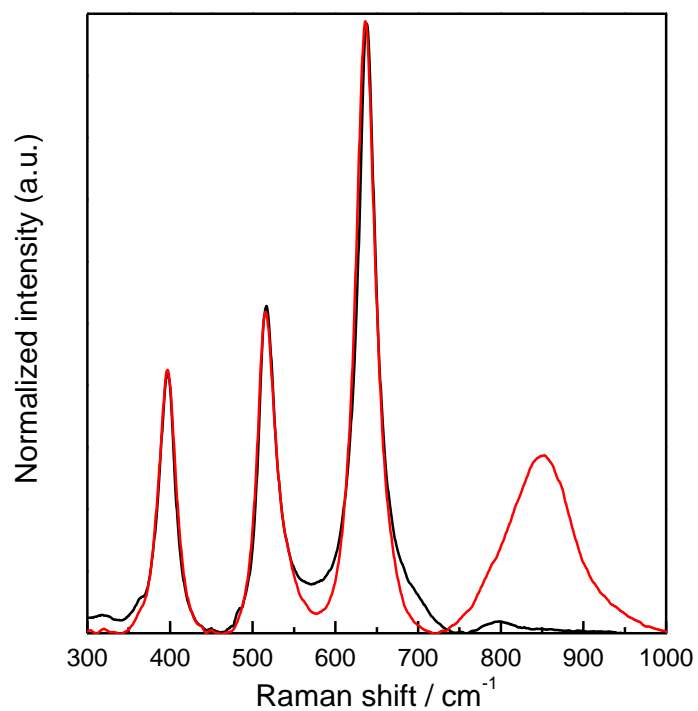


Figure S7 Normalized Raman spectra of a TiO₂ electrode surface (black) and a Cr^{III}_xO_y-deposited TiO₂ electrode (red). It was prepared by cathodic polarization in the pre-treated aqueous Cr(NO₃)₃ solution (0.14 mol L⁻¹) at -0.74 V vs. Ag/AgCl for 6 h. The spectra were normalized at 638 cm⁻¹.

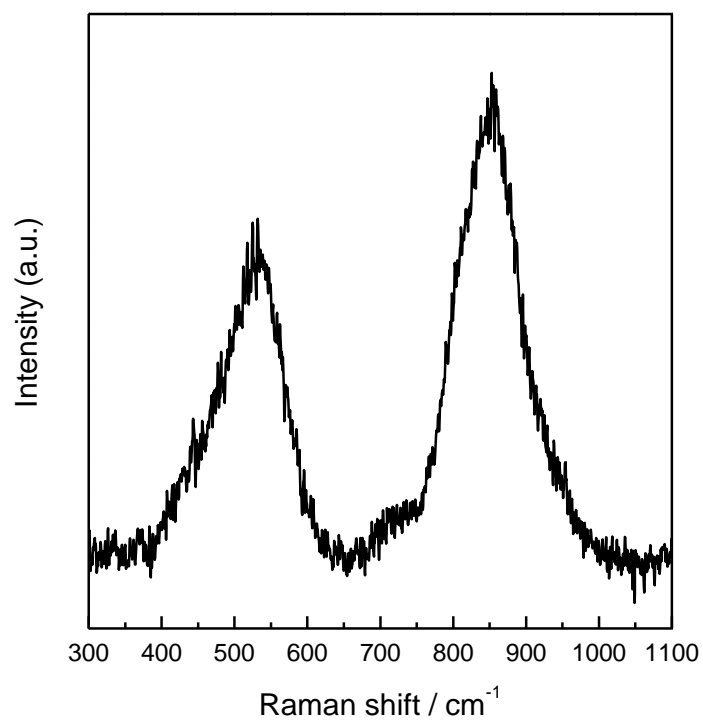


Figure S8 Raman spectrum of a Cr₂O₃ powder prepared chemically. Two major peaks at 530 cm⁻¹ and 850 cm⁻¹ can be assigned to Cr-O vibration energy of Cr₂O₃ and dehydrated Cr-O vibration of chromium-oxo compounds, respectively.

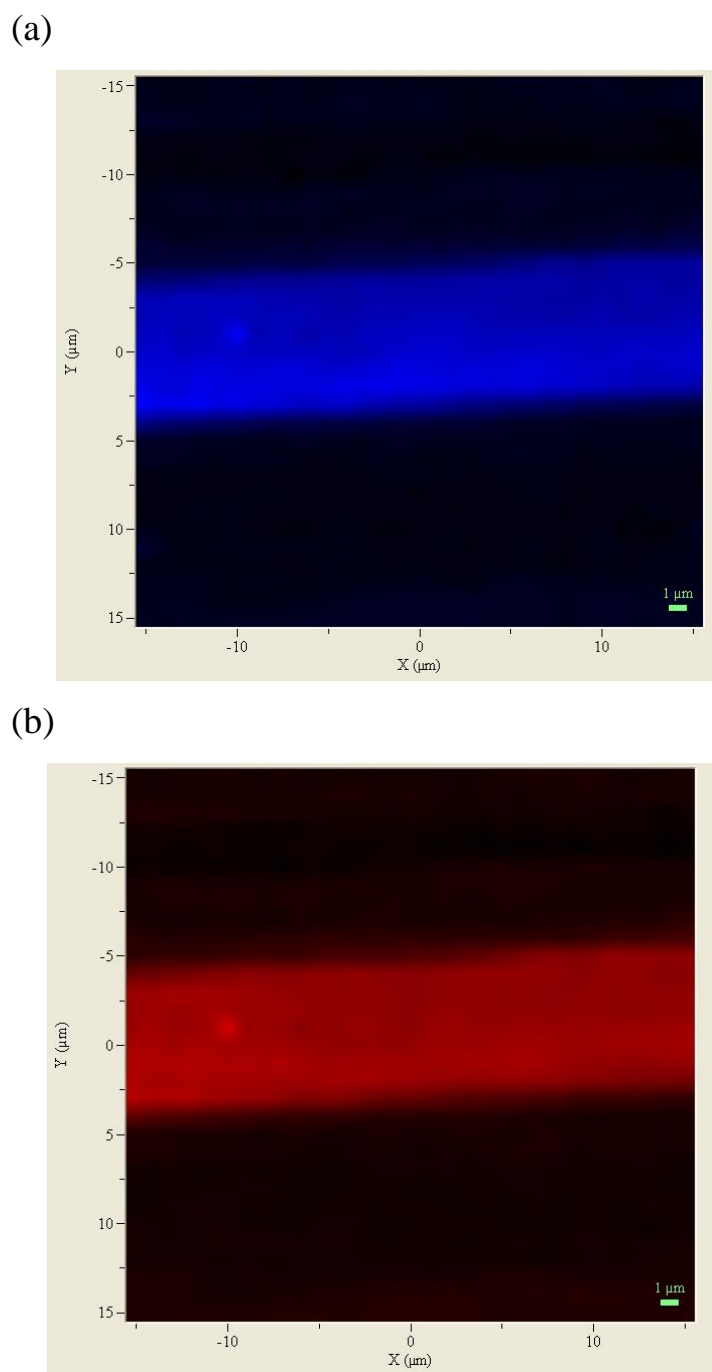


Figure S9 Raman spectral mapping images of a $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode. It was prepared by cathodic polarization in the pre-treated aqueous $\text{Cr}(\text{NO}_3)_3$ solution (0.14 mol L^{-1}) at -0.74 V vs. Ag/AgCl for 6 h. (a) Image (blue) due to $600 - 700 \text{ cm}^{-1}$ based on TiO_2 , (b) Image (red) due to $750 - 950 \text{ cm}^{-1}$ based on polychromium-oxo compounds).

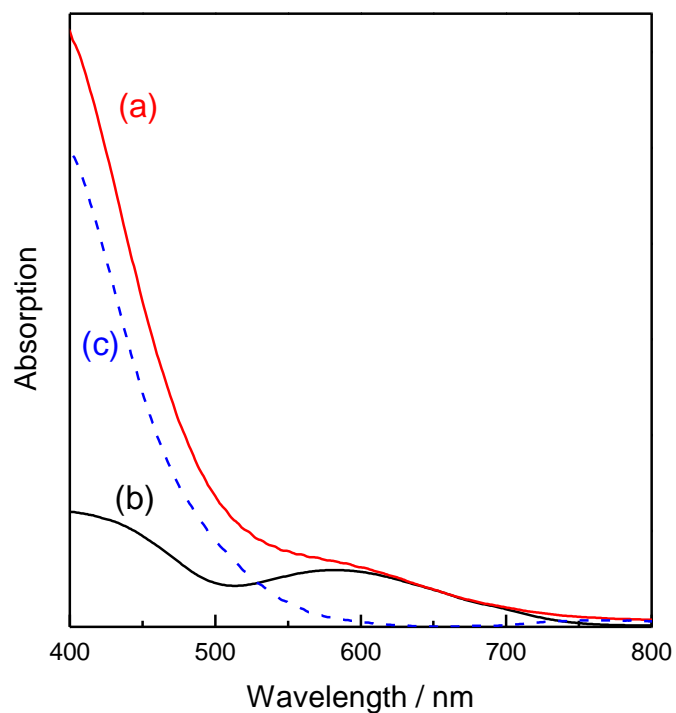


Figure S10 UV-visible diffuse reflection (DR) spectra of (a) a $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode, (b) a TiO_2 electrode with Cr_2O_3 deposited chemically. The spectrum (c) is the difference spectrum of (a) - (b), which is in agreement with the third deconvoluted spectrum assigned to the IFCT transition in Figure 1. The spectra of (a) and (b) were normalized at 660 nm.

4. Photocurrent responses and photoelectrocatalysis on the $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode.

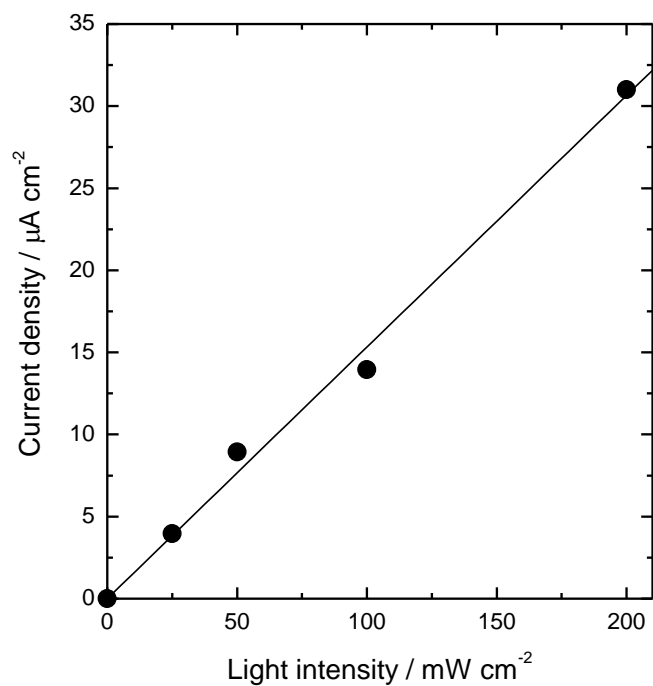


Figure S11 Plots of the photoanodic current at -0.2 V vs. Ag/AgCl versus visible light intensity (light source: a 150 W halogen lamp with a L42 UV-cut-filter ($\lambda < 420$ nm)).

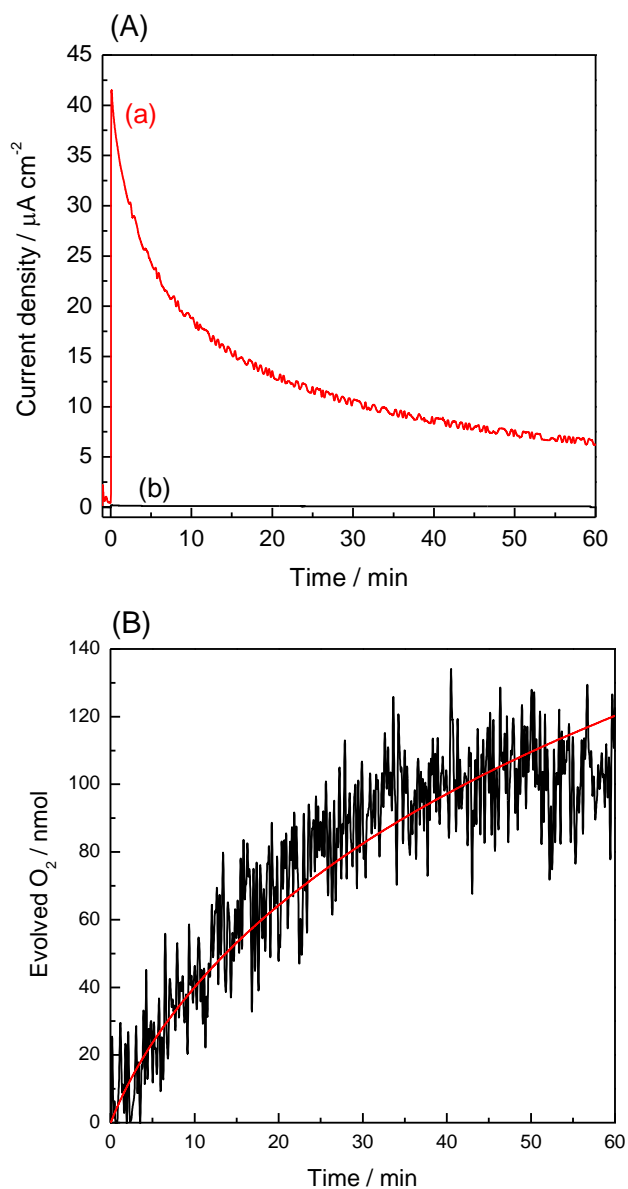


Figure S12 (A) Current density–time curve during the photoelectrolysis at -0.2 V vs. Ag/AgCl in a 0.1 mol L^{-1} phosphate buffer solution ($\text{pH} = 7.0$) using (a) a $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode and (b) a TiO_2 electrode under monochromatic light irradiation (420 nm , 15.8 mW cm^{-2}). (B) Time course of the amount of O_2 evolved during the photoelectrolysis using the $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode. The red line shows the O_2 amount calculated from the current data in Figure S12 (A).

Table S1 Summary of photoelectrocatalysis data using the $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode at various applied potentials of -0.2 V to -0.5 V vs. Ag/AgCl in a 0.1 mol L^{-1} phosphate buffer solution (pH = 7.0) under monochromatic light irradiation ($420 \text{ nm}, 15.8 \text{ mW cm}^{-2}$).

Applied potential / V vs. Ag/AgCl	Charge / mC	O_2 / μmol	F.E. $_{\text{O}_2}$ (%) ^{a)}
-0.2	50.7	0.12	94
-0.3	36.9	0.09	87
-0.4	26.1	0.06	82
-0.45	13.0	0.03	24
-0.5	4.8	N.D.	N.D.

a) Faradaic efficiency for O_2 evolution.

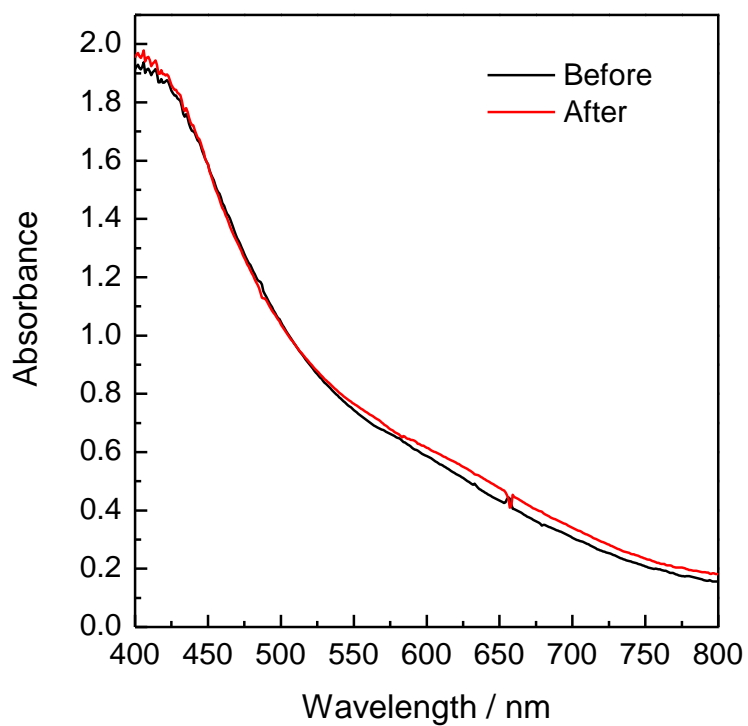


Figure S13 UV-visible absorption spectra of a Cr^{III}_xO_y-deposited TiO₂ electrode before (black) and after (red) the photoelectrocatalysis conducted at -0.2 V vs. Ag/AgCl in a 0.1 mol L⁻¹ phosphate buffer solution (pH = 7.0) under monochromatic light irradiation (420 nm, 15.8 mW cm⁻²).

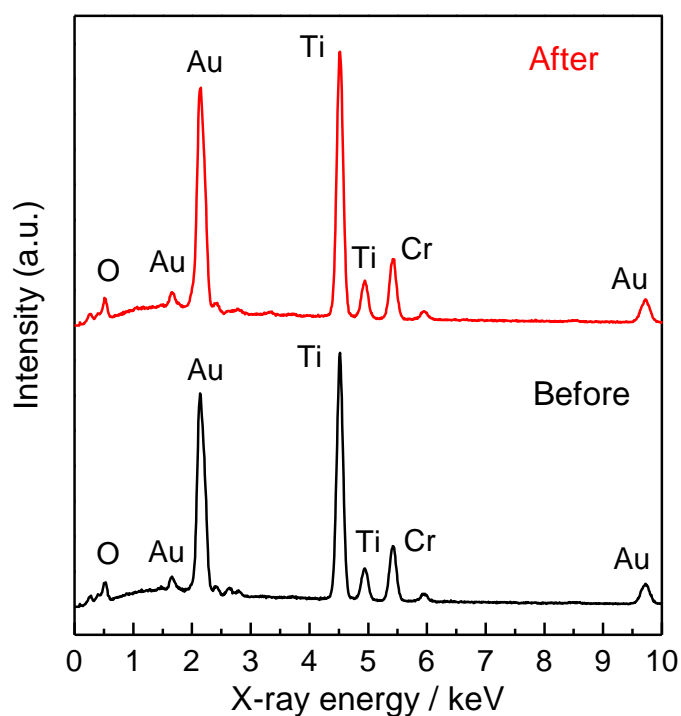


Figure S14 EDS spectra of a $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode before (black) and after (red) the photoelectrocatalysis conducted at -0.2 V vs. Ag/AgCl in a 0.1 mol L^{-1} phosphate buffer solution ($\text{pH} = 7.0$) under monochromatic light irradiation (420 nm , 15.8 mW cm^{-2}). The ratios in atom number of Cr / Ti on the polychromium oxo-electrodeposited TiO_2 electrode before and after are 49% and 48%, respectively.

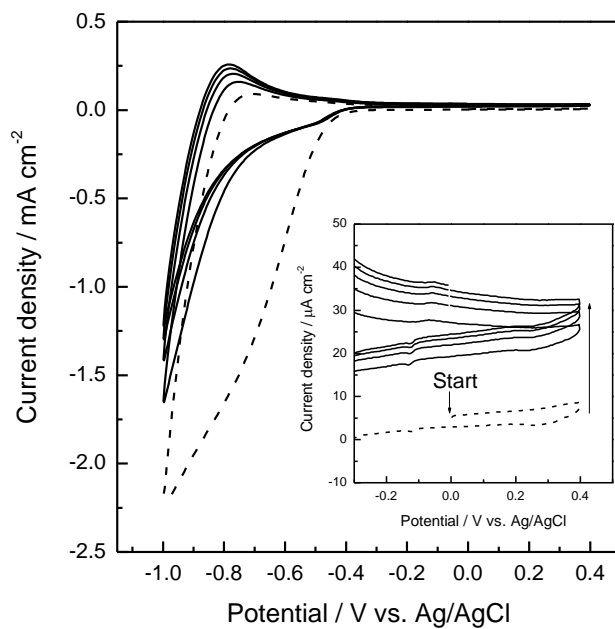


Figure S15 The repetitively-scanned CVs of the $\text{Cr}^{\text{III}}_x\text{O}_y$ -deposited TiO_2 electrode after the photoelectrocatalysis in the same buffer solution with the monochromatic light irradiated. Scan rate, 50 mV s^{-1} . A dashed line displays the first scan cycle of CV.