This is an Accepted Manuscript, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This Accepted Manuscript will be replaced by the edited and formatted Advance Article as soon as it is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about Accepted Manuscripts can be found in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard Terms & Conditions and the ethical guidelines that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these Accepted Manuscript manuscripts or any consequences arising from the use of any information contained in them.
Visible-Light-Driven Water Oxidation at a Polychromium-Oxo-Electrodeposited TiO$_2$ Electrode as a New Type of Earth-Abundant Photoanode

Masashi Kajita,$^{a}$ Kenji Saito,$^{a}$ Naoto Abe,$^{a}$ Akinori Shoji,$^{a}$ Kazuki Matsubara,$^{a}$ Tatsuto Yui$^{a}$ and Masayuki Yagi$^{a,b}$

A polychromium-oxo-deposited TiO$_2$ electrode was fabricated as an earth-abundant photoanode for visible-light-driven water oxidation by a simple electrochemical technique. The photocatalytic water oxidation could occur based on a specific interfacial charge transfer (IFCT) from a Cr$^{III}$ to the TiO$_2$ conduction band.

An artificial photosynthetic device has been attracting much interest as one of the promising clean energy-providing systems in future. Development of an efficient visible-light-driven anode for water oxidation to evolve O$_2$ is a key task to yield a breakthrough toward an artificial photosynthetic device. A great deal of effort has been devoted to develop it, and n-type semiconductor electrodes such as α-Fe$_2$O$_3$,$^{2a}$ WO$_3$,$^{2b}$ BiVO$_4$,$^{2c}$ TaON,$^{2d}$ and Co-catalyst/ZnO$^{2e}$ have been reported as the possible visible-light-driven photoanode so far. A TiO$_2$ electrode is one of the most promising photoanodes due to its notable stability and a lot of accumulated knowledge. Although a TiO$_2$ electrode exhibits a UV light response, chemical adsorption of molecular dyes on the TiO$_2$ electrode surface provides a visible light response, as known especially in dye-sensitized solar cells.$^{3}$ Visible-light-assisted water oxidation was generated at the TiO$_2$ electrode by adsorbing a Ru dye linked with IrO$_2$ colloid as a water oxidation catalyst.$^{4}$ The internal quantum efficiency for water oxidation was reported to be ~0.9% at 450 nm under 0 mV vs Ag/AgCl,$^{4b}$ and recently improved to be 2.3% (450 nm) by loading an electron mediator moiety on the IrO$_2$ colloid surface under the same conditions.$^{4b}$ The Ru dye-sensitization mechanism was extended to the other water oxidation catalyst systems of Mn-based catalysts$^{5}$ Ru complexes$^{5}$, and polyoxometalate$^{5}$ to establish light-driven O$_2$ production. However, from the viewpoint of industrial application in future, the use of earth-abundant elements and more simple methods were required for electrode preparation. Herein we fabricate a polychromium-oxo-deposited TiO$_2$ electrode as a precious element-free and visible-light-driven photoanode by a simple electrochemical technique based on the surface modification on a TiO$_2$ electrode. We report a unique electrode fabrication and photoanodic performance of visible-light-driven water oxidation.

A Cr(NO$_3$)$_3$ aqueous solution was pre-treated at -0.74 V vs. Ag/AgCl using a Pt electrode for 2 h to cause the electrode preparation faster$^4$, and then an anatase TiO$_2$ electrode was cathodically polarized at the same potential in the pre-treated solution for 6 h to form the brown deposit on the TiO$_2$ electrode. The brown deposit was not formed using the aqueous solutions of CrCl$_3$, Cr$_3$(SO$_4$)$_2$, and NaNO$_3$ instead of Cr(NO$_3$)$_3$. To understand the specific electrodeposition from the Cr(NO$_3$)$_3$ solution, the UV-visible absorption and Raman spectra of the Cr(NO$_3$)$_3$ solution were measured. The UV-visible absorption spectral change of the Cr(NO$_3$)$_3$ solution during cathodic polarization displayed that an intense absorption band at 360 nm is generated with an isosbestic point at 540 nm in contrast to no spectral change in the cases using CrCl$_3$, Cr$_3$(SO$_4$)$_2$, and NaNO$_3$ (Figure S1). The Raman spectra of the Cr(NO$_3$)$_3$ solution after the 2 h electrolysis at -0.74 V vs. Ag/AgCl exhibited a peak at 900 cm$^{-1}$, in addition to 714 cm$^{-1}$ and 1042 cm$^{-1}$ for NO$_3^-$ bending and symmetric stretching vibrations, respectively in a range of 600 ~ 1500 cm$^{-1}$ (Figure S2). The peak at 900 cm$^{-1}$ is assigned to the Cr-O vibration (890~904 cm$^{-1}$) of hydrated polychromium-oxo species.$^{9}$ The reduction of NO$_3^-$ ions is known to generate OH$^-$ according to eq. (1)$^{10}$, and it could be catalysed by Cr$^{III}$ ions as Lewis acid. Electrochemically formed OH$^-$ are supposed to react with Cr$^{III}$ ions near the electrode surface to generate polychromium-oxo species in solution.

$$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad (1)$$

In cyclic voltamogram (CV) of the pre-treated solution using an anatase TiO$_2$ electrode, a reduction wave was given at -0.39 V vs. Ag/AgCl (Figure S3) with the brown deposit formed on the TiO$_2$ electrode surface. When an ITO or a Pt electrode was used for the same CV measurement, neither was the reduction peak at -0.39 V given, nor being the deposit observed on the electrode surface.
suggests the special electrodeposition of the brown deposit onto the TiO\textsubscript{2} surface.

The distinguishable difference in the SEM image was not observed between the surfaces of the TiO\textsubscript{2} electrode with brown deposit and the neat TiO\textsubscript{2} electrode (Figures S4a and b). Presumably, TiO\textsubscript{2} particles could be covered with a thin layer of small-size brown deposit (< 50 nm). The SEM image of its cross section indicated 8 µm of the film thickness of the TiO\textsubscript{2} electrode with brown deposit under the typical preparation conditions (Figure S4c). The geometric film thickness of a TiO\textsubscript{2} electrode was hardly changed before and after formation of brown deposit for SEM observation. Energy dispersive X-ray spectroscopic (EDS) data clearly showed the presence of chromium in the brown deposit, and the molar ratio of Ti:Cr was 1:0.49 on the electrode surface (Figure S5). The amount of deposited chromium was measured to be 6.4 µmol cm\textsuperscript{-2} under the typical preparation conditions using an inductively coupled plasma mass spectrometry technique. Chromium in the deposit was also indicated by the X-ray photoelectron spectroscopy spectra giving the peaks at 585.7 and 575.9 eV, assigned to Cr 2p\textsubscript{3/2}, respectively (Figure S6). The binding energy (575.9 eV) agrees well with Cr\textsuperscript{III}\textsuperscript{2+} binding to an oxygen atom (Cr\textsubscript{2}O\textsubscript{3} : 576.0 eV), but with neither binding energies of the starting material (Cr\textsubscript{3+}O\textsubscript{2} : 577.3 eV), Cr\textsubscript{3+} hydroxide (Cr(OH)\textsubscript{3} : 577.3 eV) nor Cr\textsuperscript{IV} oxide (CrO\textsubscript{2} : 578.9 eV). This suggests that Cr\textsuperscript{III} oxo species are deposited on the electrode. The Raman spectrum of the brown deposited-TiO\textsubscript{2} surface showed a peak at 850 cm\textsuperscript{-1} in addition to three intensive peaks based on anatase TiO\textsubscript{2} in a range of 300 ~ 1000 cm\textsuperscript{-1} (Figure S7). The Raman spectrum of Cr\textsubscript{2}O\textsubscript{3} being chemically prepared exhibited two peaks at 550 and 850 cm\textsuperscript{-1}, the former of which can be assigned to Cr\textsuperscript{III} O vibration energy of Cr\textsubscript{2}O\textsubscript{3},\textsuperscript{12} the latter being the dehydrated Cr-O vibration of chromium-oxo compounds\textsuperscript{12b} (Figure S8). These XPS and Raman data suggest that the polychromium-oxo (Cr\textsubscript{3}O\textsubscript{2}) species with dehydrated Cr-O sites was electrodeposited on the electrode, but it is not neat Cr\textsubscript{2}O\textsubscript{3} because of no peak around 550 cm\textsuperscript{-1} in the Raman spectrum (Figure S7). Raman spectral mapping analyses of the cross section of the film confirmed that the Cr\textsubscript{3}O\textsubscript{2} species are uniformly deposited in the TiO\textsubscript{2} film from the ITO interface to the film surface (Figure S9).

The UV-visible absorption spectrum of the Cr\textsuperscript{III}O\textsubscript{2}-deposited TiO\textsubscript{2} electrode exhibited a wide range of light absorption in a visible region of 400 ~ 800 nm (red solid line in Fig. 1A), in contrast to almost no visible absorption for the neat TiO\textsubscript{2} electrode (black solid line). It can be deconvoluted to at least three absorption bands. The first and second bands exhibit the absorption maximum at 600 and 460 nm, which can be assigned to d-d transitions from \textit{A}_{\text{g}}\textsuperscript{2} to \textit{T}_{\text{g}}\textsuperscript{2} and to \textit{T}_{\text{g}}\textsuperscript{1g}, respectively\textsuperscript{13}. The third one is at a shorter wavelength region than the others and provides an absorption edge at 560 nm. It could be assigned to the IFCT\textsuperscript{14a} from a 3d level of the deposited Cr\textsuperscript{III} to TiO\textsubscript{2} CB because the absorption edge at 560 nm (2.2 eV) is close to the transition energies from Cr\textsuperscript{III} 3d level to TiO\textsubscript{2} CB for rutile TiO\textsubscript{2} with Cr\textsuperscript{III}-doping (2.2 eV)\textsuperscript{15} and grafting (2.1 eV).\textsuperscript{14c} The Cr\textsubscript{3}O\textsubscript{2}-deposited TiO\textsubscript{2} electrode was compared with Cr\textsubscript{2}O\textsubscript{3} deposited chemically on a TiO\textsubscript{2} substrate in the UV-visible diffuse reflectance spectrum (Figure S10). The difference between them can be interpreted by contribution of the third deconvoluted spectrum assigned to the IFCT transition in Fig 1A. This result is consistent with the specific electrodeposition onto the TiO\textsubscript{2} surface, as suggested in the CV data (Figure S3).
Photoelectrolysis was conducted in a 0.1 mol L⁻¹ phosphate buffer solution (pH = 7.0) at -0.2 V vs. Ag/AgCl under monochromatic light irradiation (420 nm, 15.8 mW cm⁻²). For TiO₂ electrode, the current value during the photoelectrolysis was 0.19 ~ 0.08 µA cm⁻², and O₂ was not evolved during the 1 h catalysis. The photocurrent density of 42 µA cm⁻² was generated at the initial stage, though it decreased to 7 µA cm⁻² (17%) during the 1 hour photoelectrolysis (total charge 50.7 mC) using the Cr³⁺O₂⁻-deposited TiO₂ electrode (Figure S12(A)). The gas in a headspace of the photoelectrochemical cell was analysed either by an optical O₂ sensor during the photoelectrolysis (Figure S12(B)) or by a gas chromatograph after photoelectrolysis. The amount of O₂ evolved was 0.12 µmol cm⁻², corresponding to Faradaic efficiency of 94%. O₂ evolution was observed over -0.45 V vs. Ag/AgCl. (Table S1) This result demonstrates that water is oxidized to O₂ by visible light. Initial internal quantum efficiency for oxygen evolution (ΦΟ₂) was 0.91% at 420 nm and -0.2 V vs Ag/AgCl. The UV-visible spectroscopic and EDS data corroborates that the Cr³⁺O₂⁻-deposited TiO₂ electrode is unchanged before and after the electrocatalysis (Figure S13 and S14). The decrease of the photocurrent density during the photoelectrolysis could be explained by accumulation of photogenerated holes, most possibly due to either slow hole diffusion in the Cr³⁺O₂⁻ layer to the surface or slow water oxidation at the surface. The hole accumulation is supported by the repetitively-scanned CVs of the electrode after the photoelectrolysis with the monochromatic light irradiated (Figure S15). The large cathodic current was observed below -0.4 V vs. Ag/AgCl in the first scan cycle (dashed line) due to consumption of the hole accumulated, followed by the photoanodic current at 0.4 V regenerating after the second scan cycle. (inset of Figure S15) The photoanodic current recovered to 90% of that observed before the photoelectrolysis by the five-repetitive potential scan from 0.4V to -1.0V. To conclude, the electron transfer for visible-light-driven water oxidation is shown in Fig 2. When the visible light is irradiated to the Cr³⁺O₂⁻-deposited TiO₂ electrode, the IFCT transition from a Cr 3d level of deposited Cr³⁺O₂⁻ to TiO₂ CB could be induced. The generated holes could oxidize water to evolve O₂ on the Cr 3d level, the injected electrons to CB reducing H⁺ to H₂ at the counter electrode (GC detected).

Fig. 2 Illustration of electron transfer proposed for visible-light-driven water oxidation on a Cr³⁺O₂⁻ deposited TiO₂ electrode. VB and CB are a valence band and conduction band, respectively. Red arrow shows interfacial charge transfer (IFCT) from a Cr 3d level of the deposited Cr³⁺O₂⁻ layer to TiO₂ CB.

Notes and references

a) Department of Materials Science and Technology, Faculty of Engineering, Niigata University, 8050 Ikarashi-2, Niigata 950-2181, Japan. E-mail: yagi@eng.niigata-u.ac.jp; Fax: +81-25-262-6790; Tel: +81-25-262-6790
b) PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
Electronic Supplementary Information (ESI) available: Experimental details, characterization data of the pre-treated solution and the electrode. See DOI: 10.1039/c000000x/

8. The similar electrode was prepared for 12 h without the pretreatment.
16. The cathodic current below -0.4 V is ascribed to reduction of Cr\text{III}O\text{y}
deposited and H\text{+} reduction at the TiO\text{2} surface.
17. When the control sample is calcined at 500 °C, the photocurrent was
hardly generated.