

## PAPER

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# Metal oxide plating for maximizing the performance of ruthenium(IV) oxide-catalyzed electrochemical oxygen evolution reaction†

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Hydrogen production by proton exchange membrane water electrolysis requires an anode with low over-potential for oxygen evolution reaction (OER) and robustness in acidic solution. While exploring new electrode materials to improve the performance and durability, optimizing the morphology of typical materials using new methods is a big challenge in materials science. RuO<sub>2</sub> is one of the most active and stable electrocatalysts, but further improvement in its performance and cost reduction must be achieved for practical use. Herein, we present a novel technology, named “metal oxide plating”, which can provide maximum performances with minimum amount. A uniform single-crystal RuO<sub>2</sub> film with thickness of ~2.5 nm was synthesized by a solvothermal-post heating method at an amount (x) of only 18 μg cm<sup>-2</sup> (ST-RuO<sub>2</sub>(18)//TiO<sub>2</sub> NWA). OER stably proceeds on ST-RuO<sub>2</sub>(18)//TiO<sub>2</sub> NWA with ~100% efficiency to provide a mass-specific activity (MSA) of 341 A g<sub>cat</sub><sup>-1</sup> at 1.50 V (vs. RHE), exceeding the values for most of the state-of-the-art RuO<sub>2</sub> electrodes.

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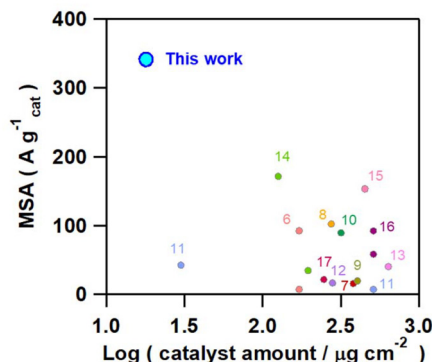
## Introduction

Electrochemical (EC) water splitting can be a favorable green process for hydrogen (H<sub>2</sub>) production.<sup>1</sup> The key step in water electrolysis is the oxygen evolution reaction (OER), involving proton-coupled four-electron transfer and O–O bond formation because of its large overpotential.<sup>2</sup> H<sub>2</sub> production by proton exchange membrane water electrolysis requires an anode with high electrocatalytic activity for OER and durability against electrolysis in acidic electrolytes.<sup>3</sup> Among various electrocatalyst materials, RuO<sub>2</sub> possesses the lowest overpotential for OER,<sup>4</sup> while only RuO<sub>2</sub> and IrO<sub>2</sub> are electronically conducting and stable at the potential where OER can occur.<sup>5</sup> Since these precious metal oxides are very expensive, devising a cost-saving strategy is also of great importance for practical use. The best indicator for the cost-performance of electrodes is the mass-

specific activity (MSA), which is provided by the product of specific activity (SA) and specific surface area (SSA) (eqn (1)).

$$\text{MSA (A g}_{\text{cat}}^{-1}) = \text{SA (A cm}^{-2}) \times \text{SSA (cm}^2 \text{ g}_{\text{cat}}^{-1}) \quad (1)$$

Considering the relation between MSA and catalyst loading amount for the RuO<sub>2</sub> electrodes reported so far for OER under acidic conditions (Fig. 1 and Table S1†),<sup>6–17</sup> a catalyst loading amount more than ~100 μg cm<sup>-2</sup> is usually necessary to obtain MSA larger than 100 A g<sub>cat</sub><sup>-1</sup>. A major challenge in EC



**Fig. 1** Relationship between mass-specific activity (MSA) and catalyst-loading amount (circles) of the RuO<sub>2</sub> electrodes reported so far for OER under acidic conditions. Blue circle expresses the data of the present study. The number expresses the reference numbers in the text.

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water splitting is to enhance the MSA by increasing the SA and SSA. Many recent studies have focused on the enhancement of the SA through a reduction in the overpotential of RuO<sub>2</sub> for OER by modifications, including doping,<sup>10,13,16,18,19</sup> hybridization with other metals,<sup>11,20</sup> and metal oxides,<sup>8,14,17,21</sup> and synthesis of multiple oxides.<sup>21–23</sup> On the other hand, even if unmodified RuO<sub>2</sub> is used as the catalyst, its MSA varies over a wide range from 6.5 to 171 A g<sub>cat</sub><sup>−1</sup>, as shown in the plots (Fig. 1). Thus, it is fundamentally important to recognize how far the MSA can be enhanced by improving the quality and optimizing the morphology of RuO<sub>2</sub> itself and the interface quality with the electrode or support to increase the SA and SSA. The development of three-dimensional electrodes has brought about a breakthrough in the areas of electrochemistry and photoelectrochemistry.<sup>24</sup> The typical TiO<sub>2</sub> nanowire array (NWA) is a fascinating anode for photoelectrochemical water splitting<sup>25,26</sup> but cannot be used as the anode for EC water splitting due to its poor electric conductivity. On the contrary, RuO<sub>2</sub> has a metallic conductivity of  $2.84 \times 10^4$  S cm<sup>−1</sup> despite being a metal oxide.<sup>27</sup> If uniform high-quality RuO<sub>2</sub> film can be formed on TiO<sub>2</sub> NWA, it would be a very promising anode for EC water splitting. Further, RuO<sub>2</sub> as well as TiO<sub>2</sub> have excellent stability, and the strong catalyst (RuO<sub>2</sub>)–support (TiO<sub>2</sub>) interaction is crucial to withstand the harsh operating conditions.<sup>28</sup> Recent studies on nanohybrids consisting of metals and metal oxides have indicated that the morphology of deposits on a substrate can be widely tuned through crystallographic interface control between them.<sup>29</sup>

Herein, we show that ultrathin single-crystalline RuO<sub>2</sub> film can be formed on TiO<sub>2</sub> NWA having a (110)<sub>RuO<sub>2</sub></sub>//(110)<sub>TiO<sub>2</sub></sub> heteroepitaxial (HEPI) relation by a solvothermal (ST)-post heating process with the RuO<sub>2</sub> loading amount and morphology controlled (ST-RuO<sub>2</sub>//TiO<sub>2</sub> NWA), where symbol // denotes the HEPI junction. The dependence of the activities of ST-RuO<sub>2</sub>//TiO<sub>2</sub> NWAs for EC and PEC OER on the RuO<sub>2</sub> loading amount was studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution. Remarkably, the ST-RuO<sub>2</sub>//TiO<sub>2</sub> NWA electrode with only  $x = 18$  stably generates OER current with an MSA of 341 A g<sub>cat</sub><sup>−1</sup>.

## Experimental

### Materials

Fluorine-doped tin(IV) oxide film-coated glass (FTO, TEC7), and Nafion film (Nafion 117, thickness = 0.007 inch) were purchased from Aldrich. Titanium tetra-*n*-butoxide (Ti(OBu)<sub>4</sub> > 97.0%), hydrochloric acid (HCl, 35.0–37.0%), methyl alcohol (CH<sub>3</sub>OH > 99.8%), ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH > 99.5%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub> > 96.0%), potassium ferricyanide (K<sub>3</sub>[Fe(CN)<sub>6</sub>] > 99.0%), potassium hexacyanoferrate(II) trihydrate (K<sub>4</sub>[Fe(CN)<sub>6</sub>]·3H<sub>2</sub>O > 99.5%), and ruthenium(IV) oxide (RuO<sub>2</sub> > 99.9%) were purchased from Kanto Chemical Co. Ruthenium(III) chloride hydrate (RuCl<sub>3</sub>·*x*H<sub>2</sub>O > 40% as Ru) was purchased from Tokyo Chemical Industry Co. All chemicals were used as received without further purification.

### Electrode preparation

Rutile TiO<sub>2</sub> NWA was synthesized according to a previously reported method.<sup>16</sup> Ti(OBu)<sub>4</sub> (0.17 mL) was dissolved in 6 M HCl (10 mL) and stirred at room temperature (298 K) for 0.5 h. The solution was put into a Teflon-reactor (volume 25 mL) and FTO (3 pieces) was immersed into the solution. The Teflon reactor was sealed in a stainless-steel autoclave and heated at 423 K for 8 h. The resulting sample was washed with distilled water and acetone and dried *in vacuo* at room temperature.

The RuO<sub>2</sub>//TiO<sub>2</sub> NWA electrodes were prepared by a solvothermal-post heating method. RuCl<sub>3</sub> (1 ~ 50 mg) was added to a mixed solution of methanol (20 mL) and water (10 mL) in a Teflon-reactor (inner volume = 50 mL) and stirred at room temperature for 0.5 h. TiO<sub>2</sub> NWA-grown FTO plates (2 pieces) were immersed in the solution, and the Teflon reactor was sealed in a stainless-steel autoclave. The autoclave was heated at 453 K for 6 h, and the resulting sample was washed with distilled water and acetone. After drying, the sample was calcined at 673 K for 10 h in air.

For comparison, RuO<sub>2</sub> NP-loaded TiO<sub>2</sub> NWA (RuO<sub>2</sub>/TiO<sub>2</sub> NWA) electrodes were prepared by the conventional impregnation method.<sup>18</sup> Commercial RuO<sub>2</sub> was dispersed into ethanol by ultrasonic irradiation for 0.5 h. After the suspension was dropped on TiO<sub>2</sub> NWA and dried at 323 K, the sample was calcined at 673 K for 10 h in air.

### Electrode characterization

To quantify the amount of Ru loading, RuO<sub>2</sub>//TiO<sub>2</sub> NWA or RuO<sub>2</sub>/TiO<sub>2</sub> NWA was immersed into 6 M HCl (10 mL) in a Teflon-reactor (volume 25 mL). The Teflon-reactor was sealed in a stainless-autoclave and heated at 473 K for 12 h. The amount of Ru dissolved into the solution was quantified by inductively-coupled plasma spectroscopy. Scanning electron microscopy (SEM) observation was carried out using a Hitachi SU8230 at an applied voltage of 20 kV. For transmission electron microscopy (TEM) observation, part of RuO<sub>2</sub>//TiO<sub>2</sub>NWA or RuO<sub>2</sub>/TiO<sub>2</sub>NWA was mechanically scraped off from the FTO substrate. TEM and high resolution-TEM images, HAADF-STEM images, and EDS mapping were obtained by means of a JEOL JEM-2100F instrument at an applied voltage of 200 kV. X-ray photoelectron spectra (XPS) were measured by means of a PHI VersaProbe 4 (ULVAC-PHI) with 15 kV and 3 mA using Al K $\alpha$  as the X-ray source. The peak of C 1s (284.6 eV) was used for energy correction. Diffuse reflectance UV-Vis-NIR spectra were measured using BaSO<sub>4</sub> as a reference ( $R_{\infty}$ ) by a UV-2600 spectrometer (Shimadzu) with an integrating sphere unit (Shimadzu, ISR-2600Plus). The spectra were transformed to absorption spectra by the Kubelka–Munk function [ $F(R_{\infty}) = (1 - R_{\infty})^2/2R_{\infty}$ ]. X-ray diffraction (XRD) patterns were obtained at 40 kV and 100 mA using a Rigaku SmartLab X-ray diffractometer.

### Electrocatalytic activity for OER

Electrochemical (EC) measurements were carried out by a two-component and three-electrochemical cell with the structure

of RuO<sub>2</sub>/TiO<sub>2</sub>NWA or RuO<sub>2</sub>/TiO<sub>2</sub>NWA (working electrode), Ag/AgCl (reference electrode)|0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution | Nafion|Pt film (counter electrode) in the dark. The active area of the working electrode was 1 cm<sup>2</sup> (1 cm × 1 cm). The electrolyte solution was deaerated by argon gas bubbling for 30 min. Linear sweep voltammetry were performed by means of a galvanostat/potentiostat (HZ-7000, Hokuto Denko) with scan rate = 20 mV s<sup>-1</sup>. The amount of O<sub>2</sub> evolved was measured by gas chromatography (GC-2010Plus with BID-detector, Shimadzu) using an Rt-Msieve 5A column (Shimadzu GLC) with helium gas flow rate = 10 mL min<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the same EC cell using a frequency response analyzer (HZA-FRA1, Hokuto Denko) built in the galvanostat/potentiostat. The measurements were carried out applying a 10 mV AC sinusoidal signal over the frequency range between 100 mHz and 100 kHz. The series resistance (*R*) and charge transfer resistance (*R*<sub>ct</sub>) were estimated by curve fitting for the Nyquist plots. The overpotential (*η*) was calculated from eqn (2) by taking the *IR* drop.

$$\eta = E - I \times R \quad (2)$$

where *R* is the ohmic resistance determined by the EIS analysis.

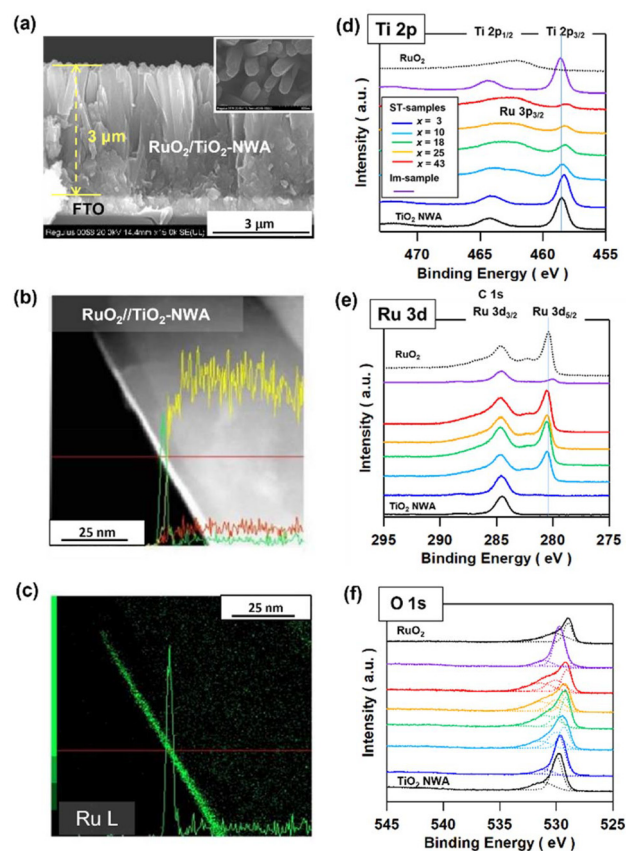
### Cyclic voltammograms

A three-electrode EC cell was fabricated with the structure of RuO<sub>2</sub>/TiO<sub>2</sub> NWA (working electrode), Ag/AgCl (reference electrode)|0.1 M NaClO<sub>4</sub> electrolyte solution containing 10 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>] and 1 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>]|Pt film (counter electrode). The active area of the working electrode was 1 cm<sup>2</sup> (1 cm × 1 cm). The electrolyte solution was deaerated by argon gas bubbling for 30 min. Cyclic voltammograms (CVs) were obtained by means of a galvanostat/potentiostat (HZ-7000, Hokuto Denko) with scan rate = 20 mV s<sup>-1</sup>.

## Results

### Electrode preparation and characterization

According to the hydrothermal method previously reported,<sup>30</sup> rutile TiO<sub>2</sub> NWs were heteroepitaxially grown from fluorine-doped tin oxide (FTO) substrate with the orientation of (001)<sub>TiO<sub>2</sub></sub>/(001)<sub>SnO<sub>2</sub></sub> (TiO<sub>2</sub> NWA).<sup>31</sup> Then, TiO<sub>2</sub> NWA was immersed into a 67% methanol aqueous solution containing various amounts of RuCl<sub>3</sub> and heated at 453 K in a Teflon-lined stainless-steel autoclave for 8 h. The samples prepared by this solvothermal (ST) reaction were calcined at 673 K for 10 h. NWs with a length of ~3 μm and a square cross-section of ~200 nm × ~200 nm were grown vertically or obliquely with respect to the FTO surface (Fig. 2a). The amount of Ru loaded on TiO<sub>2</sub> NWA was quantified by inductively-coupled plasma spectroscopy to be expressed as that of RuO<sub>2</sub> (x/μg cm<sup>-2</sup>). The *x* value of the sample increases with an increase in the content of RuCl<sub>3</sub> in the ST-reaction solution to be controlled at *x* ≤ 43 (Fig. S1†). High-angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) measurements were



**Fig. 2** (a) SEM image of the cross-section of the ST-sample (*x* = 18). The inset shows the SEM image of the surface (yellow Ti, green Ru, red O). (b and c) HAADF-STEM images of the ST-sample (*x* = 18) (yellow Ti, green Ru, red O). (d–f) XPS spectra of ST-samples (*x*), and TiO<sub>2</sub> NWA and Im-sample for comparison.

carried out for a piece of the NWs of an ST-sample (*x* = 18) (Fig. 2b and c). The TiO<sub>2</sub> NW surface is uniformly covered by an ultrathin film containing Ru with a thickness of ~2.5 nm. For comparison, RuO<sub>2</sub> was also loaded on TiO<sub>2</sub> NWA (*x* = 18) by the conventional impregnation (Im) method.<sup>32</sup> In contrast to the ST-sample, RuO<sub>2</sub> nanoparticles (NPs) with size of ~5 nm were observed on the surfaces of TiO<sub>2</sub> NWA in the Im-sample (Fig. S2†).

To identify the deposits and examine the electronic state, X-ray photoelectron spectra (XPS) were measured for the samples. In the Ti 2p XPS for an unmodified TiO<sub>2</sub> NWA, two signals are located at binding energy = 458.6 eV and 464.3 eV due to the emission from the Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> orbitals of TiO<sub>2</sub> (Fig. 2d).<sup>33</sup> After the ST-reaction, the Ti2p<sub>3/2</sub> signal rapidly weakens with an increase in *x* and shifts to a lower binding energy, while a broad signal appears at about 463 eV due to the emission from the Ru 3p<sub>3/2</sub> orbital of RuO<sub>2</sub><sup>34</sup> at *x* ≥ 10. A similar redshift in the binding energy of the Ti 2p<sub>3/2</sub> signal was reported previously in the growth of RuO<sub>2</sub> films on TiO<sub>2</sub>(110) by physical vapor deposition at 600 K.<sup>35</sup> The authors attributed this result to the formation of a Schottky barrier at the junction by measuring the valence band spectra.

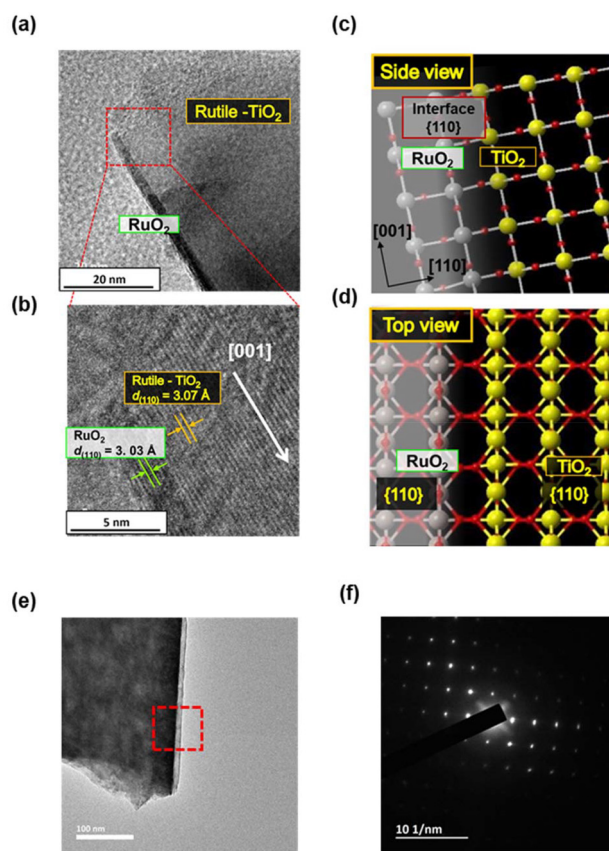


Meanwhile, the Ti  $2p_{3/2}$  signal intensities of the Im-sample at  $x = 3$  remain almost unchanged compared to that of the unmodified TiO<sub>2</sub> NWA. In the Ru 3d-XP spectra of the ST-samples (Fig. 2e), the emission from the Ru  $3d_{5/2}$  orbital is observed at 280.5 eV, which is in agreement with the value reported for the RuO<sub>2</sub>(110) surface,<sup>36</sup> and the signal intensifies with an increase in  $x$ . In the O 1s spectra (Fig. 2f), TiO<sub>2</sub> and RuO<sub>2</sub> have main signals at 529.8 eV and 529.0 eV due to the emission from the lattice oxygen, respectively, and a broad signal at about 531.5 eV tentatively assigned to the surface OH groups. For the ST samples, the ratio of the RuO<sub>2</sub> signal intensity to TiO<sub>2</sub> signal intensity ( $I_{\text{RuO}_2}/I_{\text{TiO}_2}$ ) increases with increasing  $x$  in the range of  $x \leq 18$  but tends to decrease beyond that (Table S2†). In addition, the O 1s binding energy of the ST-sample gradually shifts to lower energy from the value of TiO<sub>2</sub> to that of RuO<sub>2</sub>. On the contrary, the binding energy of the Im-sample is close to the value of TiO<sub>2</sub>. These results are consistent with the TEM observation that uniform RuO<sub>2</sub> films are formed on the surface of TiO<sub>2</sub> NWA in the ST-sample with  $x \geq 10$ , whereas RuO<sub>2</sub> NPs are sparsely precipitated on the surface in the Im-sample. The decrease in the  $I_{\text{RuO}_2}/I_{\text{TiO}_2}$  ratio in the ST-sample at  $x > 18$  suggests that if the RuO<sub>2</sub> film is too thick, it may cause degradation of the film quality due to cracks.

### Interface analysis

High resolution (HR)-TEM analysis was further performed for an NW of the ST-sample ( $x = 18$ ) to scrutinize the state of junction between RuO<sub>2</sub> and TiO<sub>2</sub> (red square part in Fig. 3a). The TiO<sub>2</sub> NW is a single crystal growing in the [001] direction with the (110) facets on the large-area side walls, as previously reported (Fig. 3b).<sup>31</sup> Interestingly, a uniform film with a thickness of  $\sim 2.5$  nm is formed on the TiO<sub>2</sub>(110) surface, and the  $d$ -spacing of 3.03 Å matches with the RuO<sub>2</sub>(110) interplanar distance. Also, the surface of TiO<sub>2</sub> is covered with a single-crystal RuO<sub>2</sub> film with a (110)<sub>RuO<sub>2</sub></sub>//(110)<sub>TiO<sub>2</sub></sub> orientation (Fig. 3b and Fig. S3†).

Both rutile TiO<sub>2</sub> and RuO<sub>2</sub> belong to the tetragonal crystal system ( $P4_2/mnm$ ), and the lattice constants are  $a = 4.5933$  Å and  $c = 2.9592$  Å for TiO<sub>2</sub> (ICDD no. 00-021-1276) and  $a = 4.4968$  Å and  $c = 3.1049$  Å for RuO<sub>2</sub> (ICDD no. 01-088-0286). There are only small  $a$ -axis and  $c$ -axis mismatches ( $\{(a_{\text{RuO}_2} - a_{\text{TiO}_2})/a_{\text{TiO}_2}\} \times 100$ ) of  $-2.1\%$  and ( $\{(c_{\text{RuO}_2} - c_{\text{TiO}_2})/c_{\text{TiO}_2}\} \times 100$ ) of  $+4.9\%$  between RuO<sub>2</sub> and TiO<sub>2</sub>, respectively. A HEPI junction model constructed using the bulk crystal dimensions for each component indicates that a single-crystalline RuO<sub>2</sub> film can be formed on the rutile TiO<sub>2</sub> surface with the (110)<sub>RuO<sub>2</sub></sub>//(110)<sub>TiO<sub>2</sub></sub> orientation (Fig. 3c and d). Further, selected area electron diffraction (SAED) was measured for TiO<sub>2</sub> NW covered by the RuO<sub>2</sub> film (red square part in Fig. 3e). A clear spot pattern is observed in the SAED pattern (Fig. 3f), further supporting the conclusion that single-crystal RuO<sub>2</sub> films are formed on the side walls of the single crystal TiO<sub>2</sub> NWA with the orientation. Thus, the formation of the strong interfacial Ru–O–Ti bonds may also contribute to the shift in the Ti  $2p_{3/2}$ -XPS signal toward lower binding energy (Fig. 2d). The sample with an



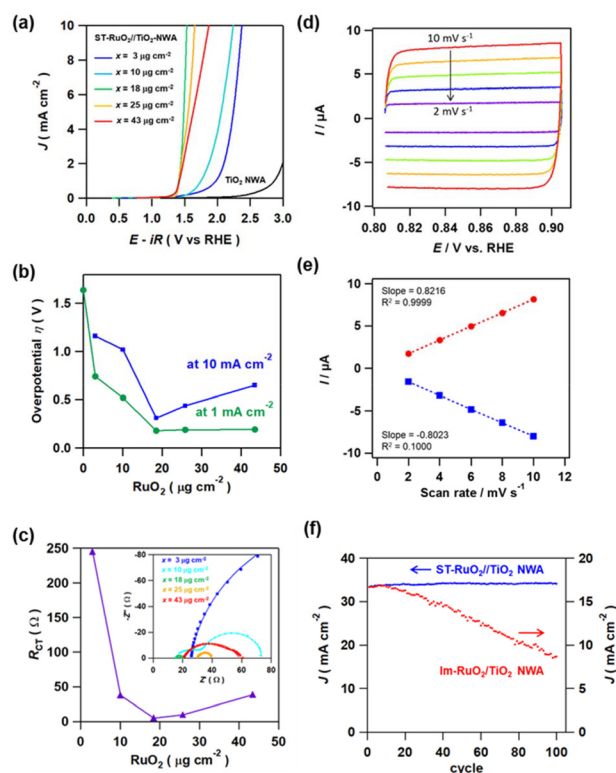
**Fig. 3** TEM image (a) and HR-TEM image (b) of RuO<sub>2</sub> ( $x = 18$ )-deposited TiO<sub>2</sub> NW. Side view (c) and top view (d) of the interface model between RuO<sub>2</sub> and rutile TiO<sub>2</sub>. TEM image (e) and (f) SAED pattern of the sample with at  $x = 18$ , respectively.

RuO<sub>2</sub>-loading amount of  $x$  ( $\mu\text{g cm}^{-2}$ ) is designated as ST-RuO<sub>2</sub>( $x$ )/TiO<sub>2</sub> NWA below.

On the other hand, in the Im-sample ( $x = 18$ , Fig. S2†), there are some aggregates of RuO<sub>2</sub> NPs, and part of them do not appear to be in direct contact with the TiO<sub>2</sub> NW surface (Im-RuO<sub>2</sub>/TiO<sub>2</sub> NWA).

### Electrocatalytic activity for OER

The OER polarization curves of TiO<sub>2</sub> NWA, Im-RuO<sub>2</sub>(18)/TiO<sub>2</sub> NWA, and ST-RuO<sub>2</sub>( $x$ )/TiO<sub>2</sub> NWAs were measured in 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution in the dark. Electrode potential ( $E$ ) was corrected to compensate the effect of solution resistance ( $R$ ) determined by electrochemical impedance spectroscopy (EIS) measurements (*vide infra*) and expressed with respect to the reversible hydrogen electrode ( $E - iR$ ,  $E_{\text{corr}}$  vs. RHE) unless otherwise noted. The amount of O<sub>2</sub> evolved over the ST-RuO<sub>2</sub>(18)/TiO<sub>2</sub> NWA electrode ( $n_{\text{O}_2}$ ) was quantified by gas chromatography. The  $n_{\text{O}_2}$  increases linearly with electrolysis time ( $t_e$ ), confirming that the OER proceeds at a constant rate of  $1.86 \mu\text{mol min}^{-1}$  and a faradaic efficiency of  $\sim 100\%$  (Fig. S4†). ST-RuO<sub>2</sub>( $x$ )/TiO<sub>2</sub> NWAs show much higher activity for OER compared to unmodified TiO<sub>2</sub> NWA and Im-RuO<sub>2</sub>/TiO<sub>2</sub> NWA (Fig. 4a and Fig. S5†). The overpotential for OER ( $\eta$ )



**Fig. 4** (a) OER polarization curves of  $\text{TiO}_2$  NWA and  $\text{ST-RuO}_2(x)/\text{TiO}_2$  NWAs in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte solution in dark. (b) Overpotential ( $\eta$ ) of  $\text{ST-RuO}_2(x)/\text{TiO}_2$  NWAs for OER as a function of  $x$ . (c) Charge transfer resistance obtained by electrochemical impedance analysis for  $\text{ST-RuO}_2(x)/\text{TiO}_2$  NWAs as a function of  $x$ . The inset shows the fitted Nyquist plots. (d) Non-faradaic polarization curves of  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA electrode with varying potential scan rate ( $\nu$ ). (e) Plots of current vs. scan rate. (f) Stability test for  $\text{Im-RuO}_2/\text{TiO}_2$  NWA, and  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA. CV curves were measured at a potential scan rate of  $20 \text{ mV s}^{-1}$ .

at current density =  $10 \text{ mA cm}^{-2}$  initially decreases with increasing  $x$  to reach a minimum at  $x = 18$  and then gradually increases (Fig. 4b). The minimal value of 303 mV is close to the values of 300 mV at  $x = 300$  (ref. 25 and 26) and 320 mV at  $x = 637$  (ref. 27) recently reported for  $\text{RuO}_2$ .

EIS measurements were performed, and the data was analyzed using an equivalent circuit in which charge transfer resistance ( $R_{\text{ct}}$ ) coupled in parallel with constant phase element (CFE) was connected in series with ohmic resistance ( $R$ ) (Fig. S6 and Table S3†). In the fitted Nyquist plots for the  $\text{ST-RuO}_2(x)/\text{TiO}_2$  NWA electrodes (inset in Fig. 4c), the  $R_{\text{ct}}$  corresponding to the diameter of the semicircle decreases parallelly with an increase in the OER activity to reach a minimum of  $4.9 \Omega$  at  $x = 18$  (Fig. 4c).

To gain insights into the origin of the large difference in the electrocatalytic activities between the  $\text{ST-RuO}_2(3)/\text{TiO}_2$  NWA and  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA electrodes, cyclic voltammograms (CVs) were measured in a 0.1 M  $\text{NaClO}_4$  electrolyte solution containing 10 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]$  and 1 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]$  degassed by argon bubbling (Fig. S7†). In the unmodified  $\text{TiO}_2$

NWA electrode, cathodic current is observed at a potential negative than  $\sim 0 \text{ V}$  vs. standard hydrogen electrode (SHE), but current hardly flows in the potential range from 0 V to 0.8 V since  $\text{TiO}_2$  is an n-type semiconductor. In contrast, the  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA electrode affords a couple of redox current peaks in a manner similar to that of the usual metal electrodes at a half-wave potential ( $E_{1/2}$ ) of 0.41 V close to the redox potential of  $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$  (0.36 V vs. SHE).<sup>37</sup> In the CV curve of the  $\text{ST-RuO}_2(3)/\text{TiO}_2$  NWA electrode, weak redox currents are observed. These results also support the conclusion from XPS (Fig. 2d and e) that the surface of  $\text{TiO}_2$  NWA and exposed FTO is completely covered by the  $\text{RuO}_2$  film in  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA, while the surface of  $\text{TiO}_2$  NWA is only partly covered in  $\text{ST-RuO}_2(3)/\text{TiO}_2$  NWA (Fig. S8†).

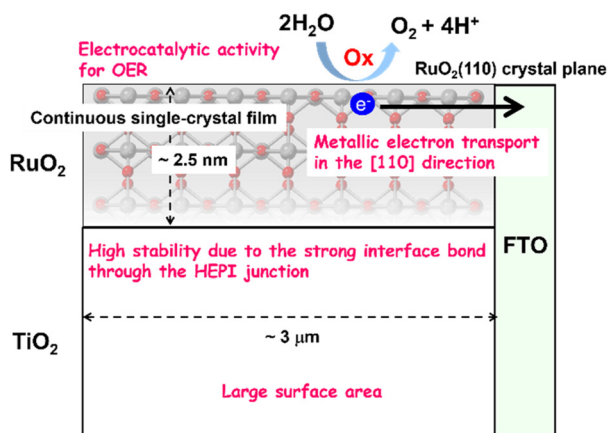
Further, non-faradaic current ( $I$ ) of  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA was measured at  $0.81 \text{ V} \leq E \leq 0.91 \text{ V}$  under varying potential scan rates ( $\nu$ ). The current increases monotonically with an increase in  $\nu$  (Fig. 4d), and the  $I$ - $\nu$  plot provides straight lines (Fig. 4e). From the slope, the electrochemically active surface area (ECSA) was calculated to be 23 using the specific capacitances of  $C_s = 0.035 \text{ mF cm}^{-2}$  in 1 M  $\text{H}_2\text{SO}_4$ .<sup>38</sup> Thus, the high electrocatalytic activity of  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA is ascribable to the uniformity, high-quality, and large actual surface area of the  $\text{RuO}_2$  film.  $\text{TiO}_2$  NWA is an important semiconductor electrode widely used in the field of photoelectrochemistry, but it is impossible to directly measure the ECSA. Making this possible is a distinctive feature of the present  $\text{RuO}_2$  plating technique from an analytical point of view.

To check the stability of the electrodes, CVs were measured at  $1.0 \text{ V} \leq E \leq 2.2 \text{ V}$  (Fig. 4f). In the  $\text{Im-RuO}_2(18)/\text{TiO}_2$  NWA electrode, the initial current at  $E = 2.2 \text{ V}$  of  $16.9 \text{ mA cm}^{-2}$  decreased to  $9.0 \text{ mA cm}^{-2}$  after 100 cycles (Fig. S9†). On the other hand, in the  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA electrode, the current of  $34.0 \text{ mA cm}^{-2}$  hardly changed during the cycles (Fig. S9†). Also, in the Ru 3d XP spectra of the  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA electrode, the signal intensity hardly changes after the 100 cycle-electrolysis (Fig. S10†). Further, the HR-TEM image of the  $\text{ST-RuO}_2(18)/\text{TiO}_2$  NWA electrode after 100-cycle electrolysis shows that a uniform  $\text{RuO}_2$  thin film with a thickness of  $\sim 2.5 \text{ nm}$  is maintained (Fig. S11†).

## Discussion

The action mechanism of the electrode is discussed using the schematic (Scheme 1). The present ST-post heating process can create uniform ultrathin single-crystal  $\text{RuO}_2$  films on the large area (110) side walls of  $\text{TiO}_2$  NWA. The strong bonding between the  $\text{TiO}_2$  NWA and the  $\text{RuO}_2$  film is caused by the HEPI junction with the  $(110)_{\text{RuO}_2}/(110)_{\text{TiO}_2}$  orientation. The loading amount and morphology of  $\text{RuO}_2$  on  $\text{TiO}_2$  NWA can be controlled by the content of  $\text{RuCl}_3$  in the reaction solution.

The activity of  $\text{ST-RuO}_2(x)/\text{TiO}_2$  NWA for EC OER steeply increases with an increase in  $x$  to reach a maximum at  $x = 18$ , where a uniform  $\text{RuO}_2$  film with a thickness of  $\sim 2.5 \text{ nm}$  is formed on the  $\text{TiO}_2$  NWA and the exposed FTO surfaces. The



**Scheme 1** Action mechanism of the ST-RuO<sub>2</sub>(18)//TiO<sub>2</sub> NWA anode for EC OER.

continuous RuO<sub>2</sub> film is in direct contact with FTO, and the Fermi energy of RuO<sub>2</sub> agrees with that of the FTO electrode. The ST-RuO<sub>2</sub>(18)//TiO<sub>2</sub> NWA electrode can output significantly higher current than the recently reported RuO<sub>2</sub> electrodes, even though the  $x$  value of the former is more than an order of magnitude smaller than the  $x$  values of the latter. Consequently, the MSA at  $E = 1.5$  V reaches  $341 \text{ A g}_{\text{cat}}^{-1}$  at only  $x = 18$  (blue circle in Fig. 1). In this system, the SA was also calculated from the values of MSA,  $x$ , and ECSA to be  $267 \mu\text{A cm}^{-2}$ , which is much larger than the value of  $64.3 \mu\text{A cm}^{-2}$  reported for RuO<sub>2</sub> (111) surface at 1.53 V in 0.1 M KOH.<sup>39</sup> Thus, the impressive MSA of ST-RuO<sub>2</sub>(18)//TiO<sub>2</sub> NWA at  $x = 18$  is ascribable to the uniformity, high-quality, and large surface area of the RuO<sub>2</sub> film working as both a good electrocatalyst for OER and electric conductor. In addition to the high-quality of the RuO<sub>2</sub> film, the strong Ti–O–Ru interfacial chemical bond (Fig. 3c and d) and the large-area interface would contribute to the high stability of the ST-RuO<sub>2</sub>(18)//TiO<sub>2</sub> NWA anode under harsh conditions. The trend is observed that the  $\eta$  at  $10 \text{ mA cm}^{-2}$  and  $R_{\text{ct}}$  somewhat increases at  $x > 18$ . Since the  $\eta$  at  $1 \text{ mA cm}^{-2}$  is almost constant at  $18 \leq x \leq 43$ , the increase in the  $\eta$  at  $10 \text{ mA cm}^{-2}$  in the range of  $x$  above 18 may be incurred by a slight deterioration of the electronic property of RuO<sub>2</sub>, as suggested by the O 1s XPS (Table S2†).

## Conclusion

The important findings of this study are as follows. (1) By virtue of the crystallographic interface design, single-crystalline RuO<sub>2</sub> films were formed on TiO<sub>2</sub> NWA using a two-step process consisting of the solvothermal reaction and post heating with the loading amount and morphology of RuO<sub>2</sub> controlled by the content of the Ru source (RuCl<sub>3</sub>). (2) This metal–oxide plating technique made it possible to measure the ECSA of TiO<sub>2</sub> NWA electrodes. (3) The activity of the ST-RuO<sub>2</sub>//TiO<sub>2</sub> NWA electrode for EC OER reached a maximum at  $x = 18$ , where the whole surface of TiO<sub>2</sub> NWA and the FTO

underlayer is covered by a uniform and continuous RuO<sub>2</sub> film with thickness of  $\sim 2.5$  nm. In addition to the remarkable OER performances with the loading of a slight amount of RuO<sub>2</sub>, the high stability renders ST-RuO<sub>2</sub>//TiO<sub>2</sub> NWA very promising as a high cost-performance anode for water splitting.

## Author contributions

S. N. and M. N. prepared the electrodes, and carried out EC experiments and the analysis, T. S. performed HR-TEM measurements and the analysis, and H. T. and H. S. supervised the experimental work and data analysis.

## Data availability

The authors confirm that the data supporting the findings of this study are available within the article and its ESI.†

## Conflicts of interest

There are no conflicts to declare.

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