Efficient overall water splitting in acid with anisotropic metal nanosheets

Dongshuang Wu1✉, Kohei Kusada1✉, Satoru Yoshioka2, Tomokazu Yamamoto2, Takaaki Toriyama3, Syo Matsumura2,3, Yanna Chen4, Okkyun Seo4, Jaemyung Kim4, Chulho Song4, Satoshi Hiroi4, Osami Sakata4, Toshiaki Ina5, Shogo Kawaguchi5, Yoshiki Kubota6, Hirokazu Kobayashi1 & Hiroshi Kitagawa1✉

Water is the only available fossil-free source of hydrogen. Splitting water electrochemically is among the most used techniques, however, it accounts for only 4% of global hydrogen production. One of the reasons is the high cost and low performance of catalysts promoting the oxygen evolution reaction (OER). Here, we report a highly efficient catalyst in acid, that is, solid-solution Ru–Ir nanosized-coral (RuIr-NC) consisting of 3 nm-thick sheets with only 6 at.% Ir. Among OER catalysts, RuIr-NC shows the highest intrinsic activity and stability. A home-made overall water splitting cell using RuIr-NC as both electrodes can reach 10 mA cm⁻²geo at 1.485 V for 120 h without noticeable degradation, which outperforms known cells. Operando spectroscopy and atomic-resolution electron microscopy indicate that the high-performance results from the ability of the preferentially exposed {0001} facets to resist the formation of dissolvable metal oxides and to transform ephemeral Ru into a long-lived catalyst.
Water electrolysis is one of the most feasible ways to provide hydrogen in the establishment of clean and renewable energy cycles, accounting around 4% global hydrogen production\(^1\). Water electrolysis involves two half-cell reactions: cathodic hydrogen evolution reaction (HER) to generate hydrogen and anodic OER to generate oxygen. HER is kinetically favoured in acid because of the high proton concentration, where current densities such as 10 mA cm\(^{-2}\) are readily achieved even at (tens of) millivolts of overpotential with a negligible amount of Pt catalysts\(^3\). The recent successes in solid polymer exchange membrane technology further accelerate water electrolysis in acid instead of conventional alkaline media\(^4\). However, the critical bottleneck lies in OER, particularly in acidic media, because most metals dissolve in the working potential region according to Pourbaix diagrams\(^5\). OER is an uphill energy transformation process involving four-proton and -electron transfers per oxygen molecule, which typically requires catalysts to work under high overpotentials and counteracts the long-term operation of catalysts. Therefore, delivering a high current density at a reduced overpotential is essential to the durability of catalysts. Although several principles have been proposed for designing OER catalysts for use in alkaline media\(^8\)–\(^11\), there are only a few reports referred to the design principles for the catalysts used in acid\(^12\). Currently, only Ir oxides show moderate stability for OER in acid\(^13\)–\(^14\), but still require high overpotentials (generally over 300 mV). In contrast, Ru is the most active OER catalyst and is nearly 5–16 times cheaper than Ir these 5 years, however, Ru has a serious degradation problem\(^15\)–\(^19\). The prevailed methods to improve the stability of Ru catalysts, such as heavy Ir doping (at least require 30 at.% of Ir)\(^20\), using thermal calcination\(^21\)–\(^22\) and strong support-metal interaction effect\(^23\), are generally at the sacrifice of activity. Operating non-degradable OER catalysts capable of operating in acid at low overpotential is one of the greatest challenges in current electrochemistry field.

Here, we report a highly active and stable Ru–Ir catalyst for overall water splitting in acid. Atomic-resolution electron microscopy and 3D tomography revealed that the obtained Ru–Ir catalyst had unique coral-like structure consisting of 3-nm-thick sheets with extended [0001] facets and composed with only 6 at.% Ir (denoted as RuIr-NC). RuIr-NC showed the lowest overpotential (165 mV) to achieve 10 mA cm\(^{-2}\) to achieve 10 mA cm\(^{-2}\) for OER in acid. Moreover, RuIr-NC achieves high mass activity and specific activity, which are 1–2 orders of magnitude higher than the reported highly active catalysts. The obtained RuIr-NC is also matched with remarkable stability that it showed no noticeable degradation throughout 122 h under a fixed geometric current density of 1 mA cm\(^{-2}\). In contrast, the comparative OER testing using the spherical RuIr catalyst shows an ordinary degradable behaviour within 1 h. Moreover, RuIr-NC displays comparable activity with commercial Pt/C toward HER. A home-made overall water-splitting cell using RuIr-NC as both electrodes achieves 10 mA cm\(^{-2}\) water-splitting current density with only 1.485 V and keeps operating over 120 h without obvious degradation, which outperforms the known cells in acidic media. One should note that the as-built overall splitting cell is less expensive than the combination of commercial Pt and IrO\(_x\) catalysts. Combining operando spectroscopy and atomic-resolution electron microscopy, we revealed that the coral-like structure with exposed extended [0001] facets is the exclusive factor that contributes the enhanced activity and stability. Although metal-based catalyst, particularly metal nanomaterials, has long been considered less stable for OER, our result shows the possibility of exploring highly efficient and stable water-splitting catalyst by optimizing the structure of the metal. Given the well-established database for controlling the structure and shape of binary or even multiple metallic nanomaterials during the past decades, our finding points out the possibility of a fast-screening process to access active and stable catalysts by using the database.

**Results and discussion**

**Catalyst synthesis and general characterization.** RuIr-NC was obtained by adding a mixture of RuCl\(_3\), nH\(_2\)O and H\(_2\)IrCl\(_6\) aqueous solutions to triethylene glycol (TEG) solution containing polyvinylpyrrolidone (PVP) at 230 °C. Transmission electron microscopy (TEM) image shows that the mean diameter of the obtained particles is 57 ± 7 nm (Fig. 1a). We further probed the atomic structure of RuIr-NC by an aberration-corrected scanning TEM (STEM) coupled with energy-dispersive X-ray spectroscopy (EDS). The high-angle annular dark-field (HAADF)-STEM image in Fig. 1b shows that the particle consists of sheet-like fragments. The 3-D tomography (Fig. 1d, Supplementary Fig. 1 and Movie 1) further confirms that the particle is assembled by anisotropically grown 2D nanosheets forming a coral-like shape. The nanosheets expose a hexagonal atomic arrangement corresponding to the (0001) hexagonal closed-packed (hcp) plane (Fig. 1c and Supplementary Fig. 2). Rietveld refinement of the synchrotron X-ray diffraction (XRD) pattern also confirmed the anisotropic growth of RuIr-NC with an extended (0001) plane (Supplementary Fig. 3). The crystal sizes estimated from the sharp peaks of (100) and (110) are 15.2(3) and 13.4(5) nm, respectively, while that from (0002) was 3.1(2) nm (Supplementary Fig. 4). The difference in the crystal size confirmed the extended (0001) plane in RuIr-NC, which is consistent with the STEM observation.

A selected area in Fig. 1c indicated by the white rectangle was further analysed to provide Ir position in the sheet and the sheet thickness (Fig. 1e). The colour represents the Gaussian peak intensity extracted from the corresponding atomic column position. The three lines denoted as I–III in Fig. 1e were quantitatively analysed to give the numbers of Ir and Ru atoms (Fig. 1f). The total number of atoms in one atomic column ranges between 6 and 9, corresponding to ~3-nm-thick sheets, which agrees well with the thickness measured from the HAADF-STEM image (Supplementary Fig. 9) and estimated crystal size from XRD (Supplementary Fig. 4). The atomic column positions containing 1 or 2 Ir atoms are denoted by the arrows (Fig. 1e), which clearly shows the random distribution of Ir atoms in the Ru hcp lattice. This result suggests the formation of a Ru-Ir solid-solution. EDS maps (Fig. 1g–i) demonstrate the homogeneous distribution of Ir and Ru atoms throughout the entire particle, which is consistent with the analyses in Fig. 1e, f. In addition, the atomic ratio of Ru and Ir estimated from EDS spectra was 0.96±0.04 (one spectrum corresponds to the particle shown in Fig. 1b was shown in Supplementary Fig. 10), which is in line with the X-ray fluorescence spectroscopy result (0.94±0.06).

As references for the catalytic tests, Ru nanoparticles (NPs), Ir NPs and Ru–Ir nanospherical catalysts (RuIr-NS) with the size of 4.9 ± 0.8, 1.9 ± 0.3 nm and 3.9 ± 0.7, respectively, were prepared (Supplementary Figs. 3, 5–8). RuIr-NS was synthesized by heat-up method, that is heating the mixture of metal precursors in TEG and PVP solution from RT to 230 °C. In contrast, RuIr-NC is obtained through a hot-injection process. It is known that the rate of surface atom diffusion is very high at an elevated temperature, which prompts the exposure of facet with lower surface energy\(^24\). Therefore, the hot-injection method would realize RuIr-NC mainly exposing the lowest energy (0001) facets\(^25\). RuIr-NS was confirmed to have the same atomic ratio and solid-solution nature as that of RuIr-NC (Supplementary Fig. 11).

**Comparison of OER activity and stability.** The OER performance of RuIr-NC was investigated in a 0.05 M H\(_2\)SO\(_4\) aqueous...
Fig. 1 Morphological and structural characterization of RuIr-NC. a Transmission electron microscopy (TEM) and b high-angle annular dark-field (HAADF)-scanning TEM image. c Atomic-resolution HAADF-STEM image from the selected area in (b) showing the extended (0001) plane. d 3D tomographic reconstruction of RuIr-NC. e The magnified image of the selected area in (c), where the colour bar represents the Gaussian intensity of the electron diffraction located at the column position. f Quantitative analysis of the Ru and Ir distribution at lines I–III in (e). The black and red numbers above each peak represent the number of total and Ir atoms in the corresponding position, respectively, and the Ir positions are noted by arrows in (e). Elemental maps showing g Ru-L (red), h Ir-M (green) and i the overlay of RuIr-NC in (b). The scale bars in (a), (b), (c), and (g–i) are 50, 20, 1, and 25 nm, respectively.
solution using a rotating disk electrode (RDE) by linear sweep voltammetry (LSV) in a procedure similar to that used in benchmark studies\(^1,6\). All the LSV curves are background current and ohmic corrected and the currents contributed from the bare RDE and carbon/Nafion mixture at higher potentials are negligible (Supplementary Fig. 12).

We compare the OER activity in three prevailed metrics, i.e., geometric activity \(j_{\text{geo}}\), mass activity \(j_{\text{m}}\), and specific activity \(j_{\text{s}}\). Geometric activity is important on the device level. With the same catalysts loading amount, RuIr-NC requires only 165 mV to achieve 10 mA cm\(^{-2}\) \(j_{\text{geo}}\) (Fig. 2a), showing much higher activity than Ir NPs (371 mV) and Ru NPs (550 mV), and the known optimal catalysts in acid (Supplementary Table 1). We must note that to avoid the overestimation of OER current due to the metal oxidation, we performed LSV from high potential to low potential (cathodic scan). Scan positively exerts a more serious oxidation/dissolution on the metals. However, the high OER activity/stability of RuIr-NC can be also reflected by the almost overlapped anodic and cathodic LSVs (Supplementary Fig. 13). The Faradaic efficiency of the RuIr-NC was 98.5% at 20 mA cm\(^{-2}\) which suggests that the oxidation current is mainly derived from OER (Supplementary Fig. 14). To put the performance of RuIr-NC into perspective, we compared its mass activity with the that of representative active catalysts listed in Supplementary Table 1. RuIr-NC is two magnitudes higher in \(j_{\text{m}}\) than those of the benchmark IrO\(_2\) and RuO\(_2\) NPs\(^{26}\) (Fig. 2b). Specifically, at 1.45 V, RuIr-NC shows a \(j_{\text{m}}\) of 796 A g\(^{-1}\)metal which is 2–4 times higher than the reported highly active catalysts\(^6,22,26,27\). The specific activity is known to be fundamentally determined by the catalysts’ EASA. The specific EASA (normalized by mass) of RuIr-NC was calculated using Cu underpotential deposition (UPD) method (Supplementary Fig. 15a–c). Remarkably, we found that at 1.45 V, the RuIr-NC showed a \(j_{\text{s}}\) of 4.4 mA cm\(^{-2}\) (Supplementary Fig. 15d), which is approximately one magnitude higher than the reported highly active catalysts with considerable stability such as IrO\(_2\)/SrIrO\(_3\) (ca. 0.67 A cm\(^{-2}\))\(^5\). From these activity evaluations, in both device-specific and material-specific figure-of-merits, RuIr-NC is no doubt the most active catalyst for OER in acid, i.e., achieving a high current density with a low overpotential.

The highly efficient RuIr-NC also combined a remarkable long-term catalytic stability. Ru NPs quickly lost the activity and showed negligible current density after the 1st LSV scan (Supplementary Fig. 16a), which is consistent with a previous study\(^19\). To evaluate the stability of Ir NPs and RuIr-NC, we adopted the chronopotentiometry (CP) measurement under a constant current density of 1 mA cm\(^{-2}\) \(j_{\text{geo}}\). As shown in Fig. 2c, a sharp rise in electrode potential indicating severe degradation was observed within 12 h for Ir NPs. In contrast, the electrode potential of RuIr-NC showed no noticeable change throughout 122 h. The RuIr-NC can sustain 40 h even under 10 mA cm\(^{-2}\) \(j_{\text{geo}}\) (Supplementary Fig. 17). Such long-term durability is unachieved among known Ru metal-based OER catalysts (Supplementary Table 1). Therefore, the RuIr-NC outperforms the best state-of-the-art OER catalyst in acidic media with a remarkably reduced overpotential and long-term stability, representing a competitive catalyst of metal-based nanomaterials.

As RuIr-NC is more active and durable for OER than the typical metal-based OER catalysts, we assumed that it was contributed by the unique nanocoral structure. This assumption is verified by comparing its catalytic performance with that of ordinary RuIr-NS. At 10 mA cm\(^{-2}\) \(j_{\text{geo}}\) RuIr-NS requires an overpotential of 242 mV (Fig. 2a), which is nearly 77 mV higher than that of RuIr-NC (165 mV). However, when scan positively, RuIr-NS showed a quite similar or slightly higher current density than RuIr-NC before 1.4 V, and its current density did not increase as sharply as that of RuIr-NC thereafter (Supplementary Fig. 13a). This suggests the serious metal oxidation/dissolution in the RuIr-NS. The stability test further shows that the activity of
RuIr-NS quickly deteriorated within 1 h (Fig. 2c), which was found in typical Ru-based catalysts17,19.

Inductively coupled plasma mass spectrometry was used to monitor the dissolution of Ru and Ir of the RuIr catalysts to validate our speculation. Almost 95 and 85% of Ru and Ir, respectively, of the RuIr-NS dissolved after five repeated polarization scans. In contrast, RuIr-NC did not dissolve as much after the second scan and had only 25% and 15% of Ru and Ir loss, respectively, even after five scans (Supplementary Fig. 16b–d). These comparative electrochemistry studies strongly demonstrated that the unique nanocoral structure is highly resistant to the dissolution during OER compared to its spherical counterpart.

Ex situ and operando characterization of RuIr-NC for OER. To explore the mechanism of the significantly enhanced OER performance of RuIr-NC compared to RuIr-NS, comprehensive spectroscopies were adopted to investigate the effect of the differences in the electronic structure and crystal size. They are generally considered to contribute to the OER performance. Hard X-ray photoelectron spectroscopy (HAXPES) with a probe depth around 20 nm was performed to give the bulk electronic structure of the RuIr catalysts (Supplementary Fig. 18). The as-prepared RuIr-NC and RuIr-NS show exactly overlapped Ru3p and Ir4f core-level spectra (Supplementary Fig. 18a, b), suggesting that they have a similar electronic structure. Lab XPS results show that the surface composition and electronic structure of Ru and Ir in the two RuIr catalysts are similar as well (Supplementary Fig. 19 and Table 4). The X-ray absorption fine structure (XAFS) was conducted to obtain the local structure of Ir in RuIr catalyst. Both the X-ray absorption near-edge spectroscopy (XANES) (Supplementary Fig. 20a) and extended XAFS (EXAFS) in Ir L3-edge (Supplementary Fig. 20b–d and Table 2) suggest that, compared with RuIr-NS, RuIr-NC is not supposed to have special Ir sites. Furthermore, the influence of crystal size effects was also excluded. An isotropic Ru–Ir catalyst was prepared by a similar heat-up method to that of RuIr-NS and subsequent high-temperature annealing under vacuum (Marked as RuIr-L). It has a similar crystal size, EASA and atomic ratio to RuIr-NC (Supplementary Figs. 21 and 22). However, it shows even lower geometric activity and similar degradation behaviour to RuIr-NS (Supplementary Fig. 23). RuIr-NC and RuIr-NS have different crystal size. However, the performance of RuIr-L could suggest that the crystal size might not be a determined reason within the study of interest. These measurements collectively suggest that the unique coral structure is the exclusive reason for the enhanced catalytic stability of RuIr-NC.

To obtain additional direct evidence of the superior stability of RuIr-NC, we conducted operando XANES to both qualitatively and quantitatively monitor the structural change in the RuIr catalysts (setup in Supplementary Fig. 24). Supplementary Fig. 25 shows Ru K-edge XANES data from open circuit potential (OCP) jumped to 1.25 V and then to 1.80 V with every 0.05 V intervals. For both catalysts, the absorption edge shifts from Ru towards RuO2 with increasing potential, suggesting an increasing oxide percentage. By using a principal component analysis algorithm and target transformation (Supplementary Figs. 26 and 27), the possible species contained in these XANES spectra were determined as two components, i.e., Ru metal and RuO2. Next, linear combination fitting (LCF) was used to evaluate the proportions of the two components (Supplementary Fig. 28 and Table 3) in order to provide a quantitative understanding of the oxidation rate. Figure 3a, b plot the percentages of Ru and RuO2 component as a function of potential during OER process of RuIr-NS and RuIr-NC, respectively. The two catalysts show quite similar XANES features below ca.1.5 V (Supplementary Fig. 29a–c), which is in accordance with their comparable activity below 1.4 V when scanned positively (Supplementary Fig. 13a). This result implies that they have similar OER-active surface structures of -O, or -OOH15,28,29. However, this tendency changed thereafter. After 1.5 V, the oxidation of RuIr-NS is sharply accelerated and only ca. 25% metallic component remained at 1.8 V, whereas the oxidation of RuIr-NC was much slower and 60% metallic component was maintained at 1.8 V (Supplementary Fig. 29d). After the operando XANES measurement, although both catalysts show only the original hcp alloy XRD pattern (Supplementary Fig. 30), core-level Ru3p and Ir4f spectra obtained by HAXPES verified the formation of oxides (Supplementary Fig. 18c, d). These results suggest that the metal oxides formed in both catalysts are amorphous. The Ru/Ir compositions of the catalysts during OER were measured by EDX (Supplementary Table 4). Before 1.4 V, the Ru/ Ir compositions in RuIr-NS and RuIr-NC samples were not changed so much. However, the percentage of Ir in RuIr-NS much more increased at 1.4 V. In contrast, the percentage of Ru and Ir in RuIr-NC did not change obviously even at 1.8 V. This implied that the dissolution rate of Ru in RuIr-NS is much higher than that of RuIr-NC. We also monitored the change of Ir L3-edge XANES during OER and found that the Ir in RuIr-NC is more resistant to oxidation compared that in RuIr-NS, which is similar to that of the result of Ru K-edge (see detailed discussion in Supplementary Fig. 20e, f). To elucidate the atomically local structure of the catalysts during OER, we measured HAADF-STEM images at three potentials:1.25 V (just prior to OER), 1.40 V (around the cross-point of the LSVs of the two RuIr catalysts, Supplementary Fig. 13a) and 1.80 V (end potential). The large area TEM images clearly demonstrate the decrease in the number and size of particles of RuIr-NS with increasing potential (Supplementary Fig. 31), which suggests the severe dissolution of RuIr-NS. The atomic-resolution HAADF-STEM images shown in Fig. 3c–e show that some parts of the remaining particles of RuIr-NS still show a crystalline metal lattice; however, most of the particles are entirely amorphous (hydro)oxides. In contrast, for RuIr-NC, the coral-like shape showing the hexagonal lattice of the hcp (0001) plane is mainly observed up to 1.80 V and size distribution of the catalyst is maintained (Fig. 3f–h and Supplementary Fig. 32). Notably, the HAADF-STEM image (Supplementary Fig. 33) shows that the growth of the amorphous oxide is affected by the metal facets: there is ca. 1-nm-thick amorphous part along with the [0001] direction whereas there is ca. 5-nm-thick along with the [1010] direction. This type of phenomenon is observed by electron diffraction and Auger spectroscopy studies on single-crystalline Ru(0001) and (100) surfaces under electrochemical and gas-phase conditions30. In addition, the (0001) facet has the lowest surface energy of hcp structures25, and thus, it would better resist oxidation than other facets. CV of RuIr-NC in Ar-saturated 0.05 M H2SO4 shows similar feature to that of single-crystalline Ru(0001) electrode (Supplementary Fig. 34), which is consistent with the STEM analyses and verifies that (0001) facet of hcp structure might protect Ru from corrosion. From the operando and ex situ measurements, the significant enhanced OER performance of RuIr-NC, can be attributed from the exposed extended [0001] facets of the unique coral structure. HER and overall water-splitting performance. Bifunctional catalysts for both HER and OER are highly desirable for practical use as an integrated water electrolyzer. In addition, Ru and Ir metals are also reported to catalyse HER31. The HER properties of RuIr-NC were investigated by using RDE in the same electrolyte as OER. The overpotential at 10 mA cm−2, gle, of RuIr-NC
was 46 mV which was lower than that of RuIr-NS (60 mV), Ir NPs (61 mV) and Ru NPs (98 mV), and comparable to that of commercial Pt/C (42 mV) (Fig. 4a). Ru or Ir NPs shows a Tafel slope of 81.0 or 42.8 mV/dec (Fig. 4b), respectively, which suggests a Volmer-Heyrovsky mechanism (Volmer: $H^+ + e^- \rightarrow H_{ad}$, 120 mV/dec, Heyrovsky: $H_{ad} + H_2O + e^- \rightarrow H_2 + OH^-$, 40 mV/dec in the theoretical calculation)\textsuperscript{32,33}, both are suffered from electron transfer. RuIr-NS has a Tafel slope of 38.3 mV/dec also showing a dominant Heyrovsky step. In contrast, RuIr-NC showed the smallest Tafel slope of 32.0 mV/dec among the synthesized catalysts. This value was close to that of commercial Pt/C (30.5 mV/dec) and suggests the efficient Tafel step ($H_{ad} + H_{ad} \rightarrow H_2$, 30 mV/dec in the theoretical calculation) (Fig. 4b). The RuIr catalysts show higher activity than monometallic catalysts, which suggests an alloying effect on the enhancement of HER activity. Moreover, theoretical calculation suggests that the 2D Ru(0001) sheets have a less negative Gibbs free energy change for hydrogen and thus higher HER activity than their powder counterpart\textsuperscript{34}. This suggests that the alloying effect and unique morphology might lead to high HER activity of RuIr-NC.

The good performance of RuIr-NC for both OER and HER allowed us to build a low-cost water electrolyzer in acid (named RuIr-NC||RuIr-NC). The voltage required to reach 10 mA cm$^{-2geo}$ is as low as 1.485 V, which outperformed the combination of commercial catalysts IrO$_2$||Pt/C (Fig. 4c and Supplementary Movies 2). Significantly, the cell is very stable at 10 mA cm$^{-2geo}$ for over 120 h of operation (<5% increase in overpotential, Fig. 4d). From these results, RuIr-NC is the most efficient bifunctional catalyst for water-splitting outperforming all known acidic electrolyzers to date (Supplementary Table S5).

In summary, we reported Ru-Ir nanocatalyst with only 6 at.% Ir as a highly efficient overall water-splitting catalyst in the acidic solution. The obtained RuIr-NC are coral-like architecture consisting of highly crystalline 3-nm nanosheets with hcp solid-
solution structure. RuIr-NC is the most efficient OER catalyst in terms of geometric activity, mass activity and specific activity and shows remarkably high stability compared to other OER catalysts in acid. The overall water-splitting cell consisting of RuIr-NC also outperform others by realizing 10 mA cm$^{-2}$geo at 1.485 V for 120 h without noticeable degradation. The control experiments on ordinary spherical Ru-Ir catalysts and spectroscopy studies revealed that the unique nanosheets with extended {0001} facets contribute to the enhanced stability and activity. Although a dynamic structure change of the OER catalyst occurs with increasing potential, our result demonstrates that finely tuning the structure of original metal particles is a promising way for designing durable OER catalysts in acid.

Methods

Synthesis of RuIr-NC. First, a solution of PVP (555 mg) dissolved in TEG (150 ml) was heated to 220 °C. Then, the mixture of RuCl$_3$·nH$_2$O ($n \approx 3$, 480.7 mg, 1.84 mmol) and H$_2$IrCl$_6$ (0.16 mmol) aqueous solution (15 ml) was added dropwise to the preheated solution. The temperature of the TEG solution was maintained at 220 °C while adding the precursors. After cooling to RT, the precipitate powder was separated from the resulting black solution by acetone follow by washing and vacuum dried process. Syntheses of other NPs are in Supporting information.

General characterization. Synchrotron XRD was measured at the BL02B2 beamline, SPring-8, Japan. The Rietveld refinement was performed using Pearson VII function with TOPAS3 software developed by Bruker AXS GmbH. The atomic percentages were determined by XRF (ZSX Primus IV, Rigaku, Japan). Bright-field TEM images were taken using an HT7700 microscope (Hitachi, Japan) operated at 100 kV. HAADF-STEM images and EDS were recorded on a JEM-ARM200F at 120 kV. Tomographic reconstruction was performed by the discrete algebraic reconstruction technique (DART) developed by Aarle et al. To determine the Ir positions and thickness, atomic column intensities were quantitatively analysed using the StatSTEM library developed by Backer et al. The single Ru and Ir atom intensity was carefully estimated based on the multislice method.

HAADF-STEM 3D tomography and Ru/Ir ratio quantitative analyses. The HAADF-STEM 3D tomography was reconstructed by a tilt series of HAADF-STEM images for the individual RuIr-NC acquired using the JEM-ARM200F at 120 kV. Tomographic reconstruction was performed by the discrete algebraic reconstruction technique (DART) developed by Aarle et al. To determine the Ir positions and thickness, atomic column intensities were quantitatively analysed using the StatSTEM library developed by Backer et al. The single Ru and Ir atom intensity was carefully estimated based on the multislice method.

Operando/ex situ XAFS. XAFS experiments of the Ru K-edge and Ir L$_3$-edge were performed using a Si(311) monochromator crystal at the BL01B1 beamline at SPring-8, Japan. All XAFS experiments were recorded in transmission mode at RT. The operando experiments were conducted with a home-made electrochemical cell (Supplementary Fig. 24). We collected the XAFS data at the OCP first and then performed quick XAFS (QXAFS) analysis during the polarization scan up to 1.8 V. To capture the change in the surface state of the catalysts, the scan rate was set as 0.05 mV/s, which is two magnitudes slower than that used in the lab experiments. For ex situ single measurements, the as-prepared materials were diluted with BN powder to make a pellet with a diameter of 7.0 or 10 mm.
XAFS analysis was performed using the Athena and Artemis program (version Demeter 0.9.26)\(^ \text{a}\). PCA and target transformation (TT) were used to determine the number and type of principal components in the sets of 13 XANES spectra (Supplementary Figs. 20–23)\(^ \text{b}\). Based on PCA, TT analyses and Roubiax diagram of Ru\(^ {\text{b}}\), Ru and RuO\(_2\) are the two components. The LCF was performed in the normalized XANES spectrum\(^ \text{b}\).

**Electrochemical measurements.** All the electrochemical measurements were conducted at RT and repeated five times to ensure reproducibility. To avoid the reaction of Ir with ClO\(_4\)\(^ {\text{−}}\) ions in OER region\(^ \text{c}\), we used 0.05 M H\(_2\)SO\(_4\) for water splitting. For the Cu UPD tests, 0.5 M H\(_2\)SO\(_4\) containing 5 mM CuSO\(_4\) were used\(^ {\text{d}}\). All OER polarization curves were background corrected to make the current before OER zero. The ohmic losses are corrected (with a percentage of 85%) based on the resistance obtained from electrochemical impedance spectroscopy (Supplementary Fig. 12). The overall water-splitting reaction of Ir with ClO\(_4\)\(^ {\text{−}}\) and oxygen electrocatalysis in water splitting and fuel cells. J. Polyoxometalate electrocatalysts based on earth-abundant metals for oxidation in hole-doped IrNiO\(_x\) core-shell electrocatalysts. Nat. Chem. Rev. 5, 13801 (2015). Shigeta, T., Honda, K., Ohashi, Y., Harada, K., & Takezoe, H. Liquid-phase synthesis of metallic ruthenium nanoparticles for oxygen evolution in alkaline solutions. J. Phys. Chem. Lett. 3, 399–404 (2012). Lin, Y. et al. Chromium-ruthenium oxide solid solution electrocatalyst for highly efficient oxygen evolution reaction in acidic media. Nat. Commun. 10, 162 (2019). Rossmeisl, J., Logadottir, A. & Norskov, J. K. Electrowater oxidation on (oxidized) metal surfaces. Chem. Phys. 319, 178–184 (2005). Roy, C. et al. Trends in activity and dissolution on RuO\(_2\) under oxygen evolution conditions: particles versus well-defined extended surfaces. ACS Energy Lett. 3, 2045–2051 (2018). Lin, W., Zeng, M., Kim, Y., Over, H. & Ertl, G. Electrochemical versus gas-phase oxidation of Ru single-crystal surfaces. J. Phys. Chem. B. 104, 6040–6048 (2000). Danilovic, N. et al. Enhancing the alkaline hydrogen evolution reaction activity through the bifunctionality of Ni(OH)\(_2\)/metal catalysts. Angew. Chem. Int. Ed. 51, 12495–12498 (2012). Shinagawa, T., Garcia-Esparza, A. & Takaneb, K. Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion. Sci. Rep. 5, 13801 (2015). Greeley, J. & Markovic, N. The road from animal electricity to green energy: combining experiment and theory in electrocatalysis. Energy Environ. Sci. 5, 9246–9256 (2012). Kong, X. et al. Free-standing two-dimensional Ru nanosheets with high activity toward water splitting. ACS Catal. 6, 1487–1492 (2016). McCusker, L., Drezel, R., Cox, D., Louter, D. & Scardi, P. Rietveld refinement guidelines. J. Appl. Cryst. 32, 36–50 (1999). Thompson, P., Cox, D. & Hastings, J. B. Rietveld refinement of Debye-Scherrer synchrotron X-ray data from Al\(_2\)O\(_3\). J. Appl. Cryst. 20, 79–83 (1987). Batenburg, K. J. & Sijbers, J. in IEEE International Conference on Image Processing. 133–136 (2011). Batenburg, B. et al. 3D imaging of nanostructures by discrete tomography. Ultramicroscopy 109, 730–740 (2009).
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Author contributions

D.W., K.K. and H. Kitagawa conceived the idea and designed the research. D.W. performed the synthesis, general characterization, and electrochemical tests. D.W., K.K., S.Y. and T.I. participated in the XAFS experiments and data analysis. T.Y., T.T. and S.M. conducted HAADF-STEM measurements and data analyses. Y.C., O. Seo, J.K., C.S., S.H. and O. Sakata performed the HAXPES measurements. S.K. and Y.K. contributed to the synchrotron XRD measurements. D.W., K.K., H. Kobayashi and H. Kitagawa discussed the results and wrote the paper. All the authors discussed and commented on the paper.

Competing interests

The authors (D.W., K.K. and H. Kitagawa) have a patent application: anisotropic nanostructure, production method therefor, and catalyst, WO 2019121744A1. D.W., K.K. and H. Kitagawa are related to this research. All other authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to D.W., K.K. or H.K.

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