Supporting Information

Emergence of High ORR activity through Controlling Local Density-of-States by Alloying Immiscible Au and Ir

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1. Methods

Theoretical methods. All of the spin polarized calculations were carried out on the Vienna ab initio simulation package (VASP),^{1,2} version 5.3.3, which is a plane wave density functional code. The electron-electron exchange and correlation interactions were described by using the generalized gradient approximation (GGA) with the form of the Perdew-Burke-Ernzerhof (PBE)³ functional. The projector augmented wave (PAW)^{4,5} method was employed to describe the interactions between the core and valence electrons. The wave functions were expanded in plane wave basis sets with a cut-off energy of 400 eV. The convergence criteria for the electronic self-consistent iteration and the ionic relaxation loop were set at values of 1×10^{-5} eV and 1×10^{-4} eV/Å, respectively. Brillouin zone integrations were performed with k-point sampling using the Monkhorst-Pack (MP)⁶ of $9 \times 9 \times 9$ and $7 \times 7 \times 1$ for the bulk and slab models, respectively. The method of Methfessel-Paxton was employed to determine the valence electron occupancies with a smearing width of 0.1 eV.

The slab models of Pt(111), Ir(111), Au(111), and Au-Ir(111) were constructed with four layers and 4×4 surface unit cells. The atoms in the bottom two layers were fixed while the rest of atoms were fully relaxed. We employed the Warren-Cowley (WC) parameter⁷ to evaluate the randomness of every slab.

The binding energy (E_B) is defined as:

$$E_B = E_{O-slab} - E_{slab} - E_O$$

where the term E_{O-slab} is the total energy for O adsorbed structures, E_{slab} is the total energy for the metal slab structures, and E_{O} is the energy of an isolated O atom.

Characterization. The atomic ratios of Au and Ir in the NPs were determined by a Rigaku ZSX Primus IV XRF instrument. TEM images were taken using a Hitachi

HT7700 operated at 100 kV. HAADF–STEM and EDX analyses were recorded on a JEM-ARM 200CF STEM instrument operated at 200 kV. Synchrotron XRD patterns were measured at the BL02B2 beamline, SPring-8. The radiation wavelength was 0.5797 Å, and the scan step was 0.006°.

Catalyst preparation. The as-prepared Au_xIr_{1-x} , Ir, Pt and Au NPs were loaded on carbon powder (Vulcan XC-72R, Cabot) by sonicating the powder mixtures in 1:4 deionized water and 2-propanol for 4 h. The amount of metal in the catalysts was fixed at 20 wt%. After collecting the carbon-loaded NP powder by the centrifugation and drying process, catalysts inks were prepared by sonicating the mixture of the catalyst powder (15.0 mg), deionized water (0.6 ml), 2-propanol (2.25 ml) and Nafion solution (0.15 ml, 5% NafionTM Dispersion Solution DE521 CS type, Wako) for 30 min. The concentration of metal in the inks was 1.0 mg/ml. A 4.0 µl aliquot of the catalyst ink was pipetted onto a polished glassy carbon surface of an RDE and dried in air to form a homogeneous thin film.

Electrochemical testing. All electrochemical tests were performed using a CHI 760e electrochemical workstation (CHI instruments, Inc., USA) connected with a RRDE-3A constant rotation system (ALS Co., Ltd, Japan). We used a conventional three electrode system: a Hg/HgO reference electrode (1.0 M NaOH), a Pt coiled wire counter electrode (57 mm in length) and an RDE (5 mm disk diameter) as a working electrode. The reference electrode was calibrated at r.t. before each test, and all potentials are reported relative to the RHE. All of the catalysts had the same metal mass weight and were loaded onto a glassy carbon RDE electrode. Each catalyst was swept from 0.04 to 1.24 V at a sweep rate of 200 mV/s for several hundreds of cycles in an Ar-saturated 1.0 M NaOH solution to obtain a stable and clean electrode surface before the ORR tests. After the electrochemical cleaning, cyclic voltammetry (Figure S13) was measured at a sweep rate of 20 mV/s. To determine the ORR activity, linear sweep voltammetry

(LSV) was measured at a sweep rate of 5 mV/s at 1600 rpm in an O_2 -saturated 1.0 M NaOH solution. All polarization curves were corrected for the *i*R drop in the solution after each scan. All of the electrochemical measurements were repeated at least 3 times to confirm the reproducibility.

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Figure S1 The comparison of the LDOS of $Au_{0.5}Ir_{0.5}(111)$ and Pt(111) surfaces. The Pt LDOS is shown as grey colour and the Au or Ir LDOS is shown as the other colours. The number indicates the position of the Au or Ir atom on the $Au_{0.5}Ir_{0.5}(111)$ surface shown in the lower left. This layer is the top layer of the 4layer slab model of the $Au_{0.5}Ir_{0.5}(111)$ surface shown in Figure S5. Dark yellow and pink spheres indicate Ir and Au atoms, respectively. The details of the structural model are explained in Figure S5.

Ir site	2	3	4	5	6	7	8	9	Ave.
<i>d</i> -band	-2.78	-2.66	-2.88	-3.00	-2.59	-2.88	-3.18	-2.84	-2.85
centre (eV)									

Table S1. *d*-band centre of Ir LDOS in of Au_{0.5}Ir_{0.5}(111) shown in Figure S1

	d-	-band center (e	eV)	Inte	egral (states at	om ⁻¹)
	TDOS	Ir LDOS	Au LDOS	TDOS	Ir LDOS	Au LDOS
Ir	-3.34			8.16		
Au _{0.2} Ir _{0.8}	-3.27	-3.19	-3.49	8.48	6.08	2.40
Au _{0.5} Ir _{0.5}	-3.24	-2.85	-3.57	8.81	4.01	4.80
Au _{0.7} Ir _{0.3}	-3.24	-2.68	-3.45	9.08	2.50	6.58
Au	-3.53			9.56		
Pt	-2.87			9.1		

Table S2. *d*-band centre and integral of total and local DOS

3. O binding energies on Ir, Pt, Au and Au_{0.5}Ir_{0.5}(111) surfaces

3. 1. Ir(111) surface

	Site	Binding energy (eV)
1	Тор	-3.97
2	Bridge (\rightarrow fcc)	-5.04
3	fcc	-5.04
4	hcp	-4.82

Table S3. Oxygen adsorption site and binding energy on the Ir(111) surface



Figure S2 (a) Side view of the 4-layer slab model of the Ir(111) surface. (b) Top view of the top layer. The numbers in (b) the top layer indicate the adsorption sites listed in Table S3. The calculated binding energies on the monometallic Ir surface are similar to those found in previous reports⁸.

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3. 2. Pt(111) surface

	Site	Binding energy (eV)
1	Тор	-2.97
2	Bridge (\rightarrow fcc)	-4.30
3	fcc	-4.30
4	hcp	-3.81

Table S4. Oxygen adsorption site and binding energy on the Pt(111) surface



Figure S3 (a) Side view of the 4-layer slab model of the Pt(111) surface. (b) Top view of the top layer. The numbers in (b) the top layer indicate the adsorption sites listed in Table S4. The calculated binding energies on the monometallic Pt surface are similar to those found in previous reports⁹.

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3. 3. Au(111) surface

	Site	Binding energy (eV)
1	1 Top	N/A
2	2 Bridge (\rightarrow fcc)	-3.01
3	3 fcc	-3.01
4	4 hcp	-2.87

Table S5. Oxygen adsorption site and binding energy on the Au(111) surface



Figure S4 (a) Side view of the 4-layer slab model of the Au(111) surface. (b) Top view of the top layer. The numbers in (b) the top layer indicate the adsorption sites listed in Table S5. The calculated binding energies on the monometallic Au surface are similar to those found in previous reports¹⁰.

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3. 4. Au_{0.5}Ir_{0.5}(111) surface

	Site	Binding energy (eV)
1	Ir top	-4.30
2	Au top	N/A
3	Ir-Ir bridge	-4.68
4	Au-Au bridge	N/A
5	Ir-Au bridge (→Ir top like)	-4.26
6	Ir ₃ fcc	-4.78
7	Ir_2Au_1 fcc (\rightarrow Ir-Ir bridge)	-4.68
8	Ir_1Au_2 fcc (\rightarrow Ir top like)	-4.20
9	Au ₃ fcc	-3.20
10	Ir ₃ hcp	-4.76
11	Ir_2Au_1 hcp (\rightarrow Ir-Ir bridge)	-4.68
12	Ir_1Au_2 hcp (\rightarrow Ir top like)	-4.20
13	Au ₃ hcp	N/A

Table S6.	Oxygen	adsorption	site and	binding	energy	on the	$Au_{0.5}Ir_{0.5}$	s(111) s	urface



Figure S5 (a) and (c) Side views of the 4-layer slab models of the $Au_{0.5}Ir_{0.5}(111)$ surface. (b) and (d) Top view of the top layers. The numbers in (b) the top layer indicate the adsorption sites listed in Table S6.

The alloy slab model was chosen as an ideal solid-solution structure given the Warren-Cowley (WC) parameter of 0^7 . Since the above model does not have an Au₃-hcp site, the binding energy of the Au₃-hcp site was obtained using another surface model giving the WC parameter of 0 (Figures 5c and d); this model also provides similar energies at other sites. The WC parameter (a_i) was calculated according to the following formula:

$$a_i = 1 - \frac{P_A^i}{C_A}$$

For a binary A–B alloy system, where P_A^i is the conditional probabilities of having B atoms as neighbours in the *i*-th coordination sphere of the substrate, C_A is the concentration of atoms. If a_i equals 0, it indicates that the alloy structure is complete randomness. If $a_i < 0$, it indicates that the A–B bonds are dominant in the alloy system

(local order or supercell), while if $a_i > 0$, it indicates that A–A bonds are dominant in the alloy system (phase-separated or clustered). Therefore, if the model has WC parameters with a value of 0, the constructed slab is a solid-solution structure.

3. 5. Au_{0.7}Ir_{0.3}(111) surface

	Site	Binding energy (eV)
1	Ir top	-4.54
2	Au top	N/A
3	Ir ₃ fcc	-5.00
4	Ir_2Au_1 fcc (\rightarrow Ir-Ir bridge)	-4.80
5	Ir_1Au_2 fcc (\rightarrow Ir top like)	-4.47
6	Au ₃ fcc	-3.35
7	Ir ₃ hcp	-4.64
8	Ir ₂ Au ₁ hcp (→Ir-Ir bridge)	-4.82
9	Ir_1Au_2 hcp (\rightarrow Ir top like)	-4.49
10	Au ₃ hcp	N/A

Table S7. Oxygen adsorption site and binding energy on the $Au_{0.7}Ir_{0.3}(111)$ surface



Figure S6 (a) and (c) Side views of the 4-layer slab models of the $Au_{0.7}Ir_{0.3}(111)$ surface. (b) and (d) Top view of the top layers. The numbers in (b) the top layer indicate the adsorption sites listed in Table S7.

The alloy slab model was chosen as an ideal solid-solution structure given the Warren-Cowley (WC) parameter of 0^7 .

3. 6. Au_{0.2}Ir_{0.8}(111) surface

Table S8. Oxygen adsorption site and binding energy on the Au_{0.2}Ir_{0.8}(111) surface

	Site	Binding energy (eV)
1	Ir top	-4.12
2	Au top	N/A
3	Ir ₃ fcc	-5.05
4	Ir_2Au_1 fcc (\rightarrow Ir-Ir bridge)	N/A
5	Ir_1Au_2 fcc (\rightarrow Ir top like)	N/A

6	Au ₃ fcc	-3.55
7	Ir ₃ hcp	-5.14
8	Ir_2Au_1 hcp (\rightarrow Ir-Ir bridge)	N/A
9	Ir_1Au_2 hcp (\rightarrow Ir top like)	-4.18
10	Au ₃ hcp	-3.72



Figure S7 (a) and (c) Side views of the 4-layer slab models of the $Au_{0.2}Ir_{0.8}(111)$ surface. (b) and (d) Top view of the top layers. The numbers in (b) the top layer indicate the adsorption sites listed in Table S8.

The alloy slab model was chosen as an ideal solid-solution structure given the Warren-Cowley (WC) parameter of 0⁷.

In all of the alloy surfaces, although the adsorption energy at Ir top site can be discussed by simple d-band centre theory, the tendency of the adsorption property at other sites such as hollow sites cannot be easily explained. In order to explain the tendency of the adsorption property, we need to consider other descriptors to be discussed elsewhere.

4. Synthesis details

Au_xIr_{1-x}NPs synthesis. In a typical synthesis of Au_xIr_{1-x} NPs (x = 0.5), poly(*N*-vinyl-2pyrrolidone) (PVP, 668.9 mg, MW \approx 40000, Wako) was dissolved in ethylene glycol (EG, 300 ml, Wako), and the solution was heated to 195 °C with magnetic stirring. Meanwhile, HAuCl₄ (94.6 mg, Aldrich) and IrCl₄•xH₂O (133.5 mg, Mitsuwa Chemicals) were dissolved in deionized water (40 ml). The precursor solution was then slowly added to the EG solution. The solution was maintained at 195 °C while adding the solution. After cooling to room temperature, the prepared NPs were separated by centrifugation. Other Au_xIr_{1-x} (x = 0.2 and 0.7) NPs were prepared by controlling the molar ratio of Au³⁺ and Ir⁴⁺ ions. The details of the synthetic conditions for Au_xIr_{1-x} NPs are summarized in Table S9.

	HAuCl ₄	IrCl ₄ •xH ₂ O	PVP
Au _{0.2} Ir _{0.8}	39.5 mg	166.4 mg	664.3 mg
Au _{0.5} Ir _{0.5}	94.6 mg	133.5 mg	668.9 mg
Au _{0.7} Ir _{0.3}	165.5 mg	66.6 mg	672.6 mg

Table S9.	The synth	etic condition	ons for A	u _x Ir _{1-x} N	٧Ps
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Ir NP synthesis. Poly(N-vinyl-2-pyrrolidone) (PVP, 55.5 mg, MW \approx 40000, Wako) was dissolved in water (25 ml), and the solution was heated to 100 °C with magnetic stirring. Meanwhile, IrCl₄•xH₂O (37.0 mg, Mitsuwa Chemicals) and NaBH₄ (56.5 mg, Wako) were dissolved in deionized water (5 ml) and EtOH (5 ml, Wako), respectively. The precursor and NaBH₄ solutions were then alternately dropped into the PVP

solution. The solution was maintained at 100 °C while adding the solution. After cooling to room temperature, the prepared NPs were separated by centrifugation.

Pt NP synthesis. Poly(N-vinyl-2-pyrrolidone) (PVP, 111.1 mg, MW \approx 40000, Wako) was dissolved in EG (100 ml, Wako), and the solution was heated to 170 °C with magnetic stirring. Meanwhile, K₂PtCl₄ (332.1 mg, Aldrich) was dissolved in deionized water (20 ml). The precursor solution was then slowly added to the EG solution. The solution was maintained at 170 °C while adding the solution. After cooling to room temperature, the prepared NPs were separated by centrifugation.

Au NP synthesis. Poly(N-vinyl-2-pyrrolidone) (PVP, 555.5 mg, MW \approx 40000, Wako) and HAuCl₄ (39.4 mg, Aldrich) were dissolved in EG (60 ml, Wako), and the solution was stirred at RT. Meanwhile, NaOH (199.9 mg, Wako) was dissolved in deionized water (2 ml). The NaOH solution was then added to the EG solution. The solution was stirred for 30 min at RT. After the reaction was over, the prepared NPs were separated by centrifugation.



Figure S8 XRD patterns of the synthesized Au, Ir and Pt NPs.

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5. Elemental analysis of the prepared Au_xIr_{1-x} NPs

The metal composition of the obtained NPs was characterized by X-ray fluorescence measurements using a Rigaku ZSX Primus IV XRF instrument. The average value was calculated from three measurements, as shown in Table S10.

	Au (at%)	Ir (at%)
Au _{0.2} Ir _{0.8}	22.9	77.1
Au _{0.5} Ir _{0.5}	50.5	49.5
Au _{0.7} Ir _{0.3}	70.0	30.0

Table S10. The atomic ratio of Au and Ir in Au_xIr_{1-x} NPs

6. TEM images and the average size of the prepared NPs



Figure S9 TEM images of (a) $Au_{0.2}Ir_{0.8}$, (b) $Au_{0.5}Ir_{0.5}$, (c) $Au_{0.7}Ir_{0.3}$, (d) Ir, (e) Pt, and (f) Au NPs. The scale bars are 20 nm.

Table S11. The average size	ze of the obtained NPs
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	Au _{0.2} Ir _{0.8}	Au _{0.5} Ir _{0.5}	Au _{0.7} Ir _{0.3}	Ir	Pt	Au
Size (nm)	5.5±1.4	7.2±1.7	9.9±2.3	1.4±0.4	5.7±0.7	7.1±1.2

7. Elemental analysis of the particle surface of Au_{0.5}Ir_{0.5} NP

The metal composition of the surface of $Au_{0.5}Ir_{0.5}$ NP was investigated by EDX point analysis using a JEM-200CF. The average composition x in Au_xIr_{1-x} was calculated to be 0.43 ± 0.13 .



Figure S10 HAADF-STEM image $Au_{0.5}Ir_{0.5}$ NP and the results of EDX point analysis. The analysed positions were marked in the HAADF-STEM image.

8. STEM analysis of $Au_{0.2}Ir_{0.8}$ and $Au_{0.7}Ir_{0.3}$ NPs



Figure S11 Scanning transmission electron microscopy of Au_{0.2}Ir_{0.8} NPs. **a**, a HAADF-STEM image. **b**, **c**, Au-M and Ir-M STEM–EDX maps (red, Au; yellow, Ir).



Figure S12 Scanning transmission electron microscopy of Au_{0.7}Ir_{0.3} NPs. **a**, a HAADF-STEM image. **b**, **c**, Au-M and Ir-M STEM–EDX maps (red, Au; yellow, Ir).

9. Elemental analysis of the prepared Au_xIr_{1-x} and Pt catalysts

The loading amount of metals on the carbon support was characterized by CHN elemental analysis. The average value was calculated as shown in Table S12.

Table S12. The loading amount of metals on the carbon support

	Au _{0.2} Ir _{0.8}	Au _{0.5} Ir _{0.5}	Au _{0.7} Ir _{0.3}	Ir	Pt	Au
wt%	21.8	24.0	23.4	23.6	25.4	21.5



Figure S13 Cyclic voltammograms of (a) $Au_{0.2}Ir_{0.8}$, (b) $Au_{0.5}Ir_{0.5}$, (c) $Au_{0.7}Ir_{0.3}$, (d) Ir, (e) Pt, and (f) Au catalysts. Black and red curves indicate the CV obtained in Ar and O₂ saturated 1.0 M NaOH solutions, respectively. The scan rate was 20 mV/sec.

Figure S14 RDE polarization curves of $Au_{0.5}Ir_{0.5}$ and monometallic catalysts at 1600 rpm in an O₂-saturated 0.05 M H₂SO₄ aqueous solution. The catalytic tests were performed in the same procedure as in 1.0 M NaOH aqueous solution case.

11. Electrochemical oxygen-reduction activities in an acidic solution



12. accelerated durability test of Au_{0.5}Ir_{0.5} catalyst

Figure S15 (a) Cyclic voltammograms of $Au_{0.5}Ir_{0.5}$ in an Ar-saturated 1.0 M NaOH aqueous solution before and after ADT. The durability test was carried out for the same sample at room temperature in an O₂-saturated 1.0 M NaOH aqueous solution with the cyclic potential sweeping between 0.65 and 0.95 V (vs RHE) at a sweep rate 100 mV/s. (b) RDE polarization curves of $Au_{0.5}Ir_{0.5}$ before and after ADT at 1600 rpm in an O₂-saturated 1.0 M NaOH aqueous solution.

Table S13. The H_{upd} peak area (Q_H) (calculated from 0.1 to 0.4 V (vs RHE)) of Au_{0.5}Ir_{0.5} catalyst before and after ADT test

	Initial	After 500 cycles	After 1,000 cycles	After 10,000 cycles
		1.03×10 ⁻⁴	1.01×10 ⁻⁴	9.84×10 ⁻⁴
$Q_{\rm H}\left({\rm C} ight)$	1.07×10 ⁻⁴	(96.7%)	(94.2%)	(92.1%)