Electronic Supplementary Information

Electroless deposition of iridium oxide nanoparticles promoted by condensation of $[Ir(OH)_6]^{2-}$on an anodized Au surface: Application to electrocatalysis of the oxygen evolution reaction

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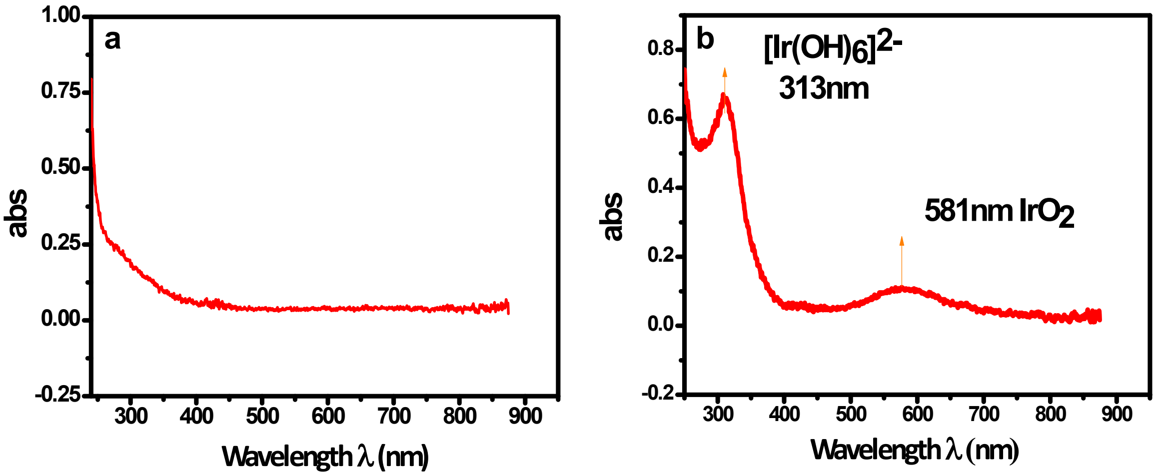
Materials and Methods

All chemicals, sodium hydroxide (A.R), iridium (III) chloride trihydrate (A.R) ($IrCl_3.H_2O$), and sulphuric acid (A.R) were purchased from Merck. The electrochemical experiments were carried out using an IVIUM Compactstat workstation. A standard three-electrode cell consisting of a 1.6 mm diameter gold disk working electrode, Hg/HgO (0.1M NaOH) and Hg/Hg_2SO_4 (0.5M H_2SO_4) as reference electrodes. (An Ag/AgCl reference electrode with a salt bridge containing saturated sodium nitrate- agar-agar gel, was employed to avoid chloride contamination in studies on the pH effect on OER), and 1cm^2 Pt foil used as a counter electrode in all voltammetric experiments. The potential values are referred to reversible hydrogen electrode, RHE (by adding 165 mV + 780 mV in 0.1M NaOH (pH 13) for Hg/HgO and 680 mV for Hg/Hg_2SO_4). (The value, 780 mV is calculated from pH 13* 59.9 mV for OER). All solutions were prepared using water purified by Milli-Q purification system (18.2 MΩ.cm) and the cell temperature was maintained at 27°C. The X-ray photoelectron spectra were collected on a Multilab2000 (Thermo Scientific UK). FE-SEM and EDAX were performed on ZEISS SUPRA-55VP model instrument.

Anodization of gold surface

For anodization of the mechanically-polished gold surface, the procedure of Nishio and Masuda[1] was used using 0.5M H_2SO_4 as the electrolyte. [Procedural details are discussed in the main text].

A



B

a

b

C

Figure S1. (A) UV-Visible spectra for $IrCl_3$ in 0.1 M NaOH (a); and $IrCl_3$ in 0.1 M NaOH after one hour (b); (B) Photograph of Au disk-Pt ring electrode (a); anodized Au disk-Pt ring electrode (b); Iridium-coated anodized Au disk-Pt ring electrode (c).

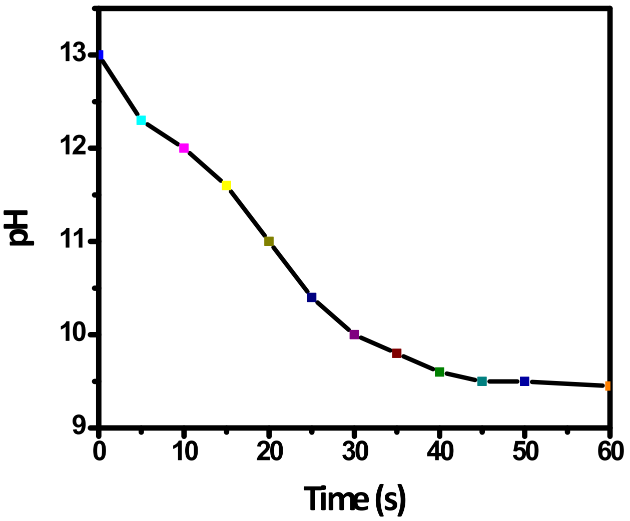


Figure S2. Time evolution of pH accompanying the formation of $[Ir(OH)_6]^{2-}$

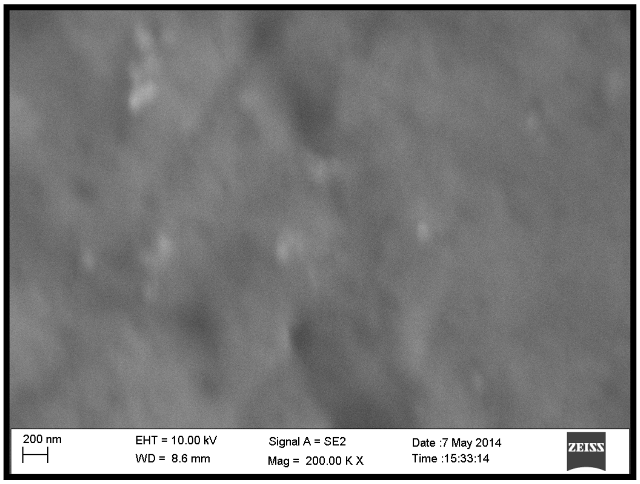


Figure S3a. FE-SEM image of bare gold surface

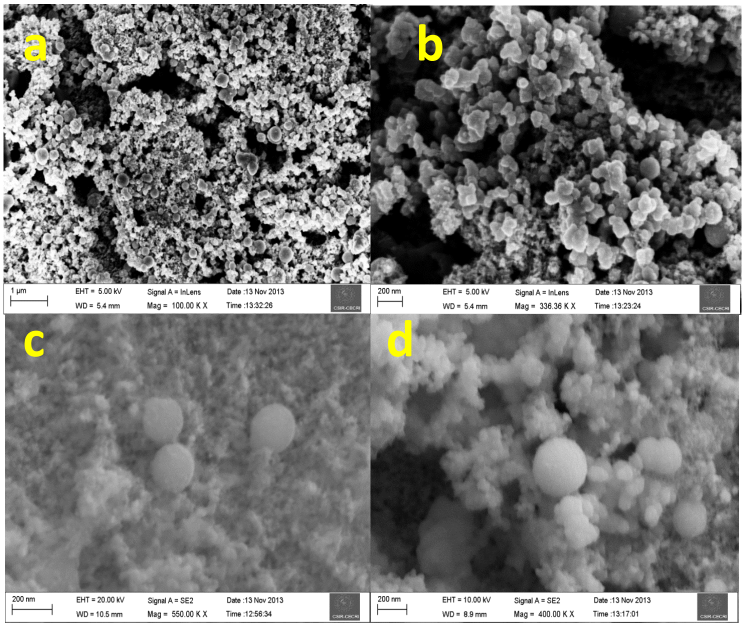
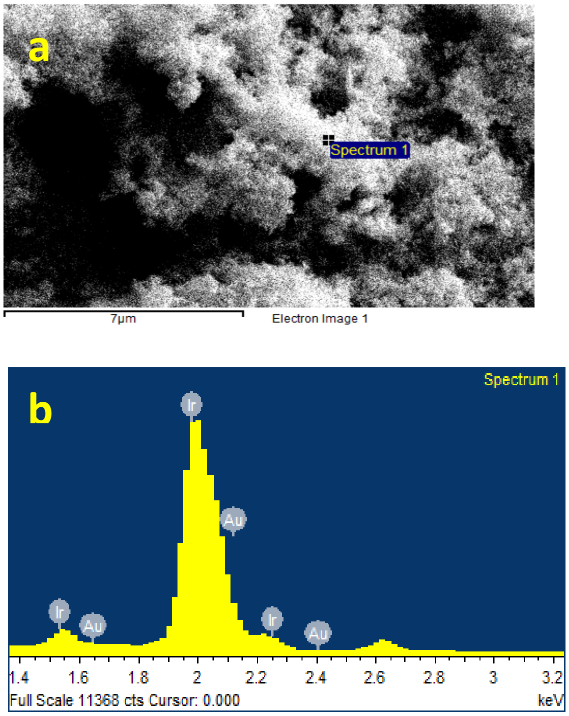


Figure S3b. FESEM images of the IrO_x/Au surface: (a) x 20k, (b) x 50k (c) x 100k (d) x 120 k



Element	Weight%	Atomic%	Compd%	Formula
Ir	52.00	21.53	60.66	IrO_2
Au	35.07	14.17	39.34	Au_2O_3
O	12.93	64.31		
Totals	100.00			

Figure S4. EDAX spectrum of IrO$_x$ coated gold surface (a) showing location in FESEM image where EDAX analysis was performed, (b) EDAX elemental composition.

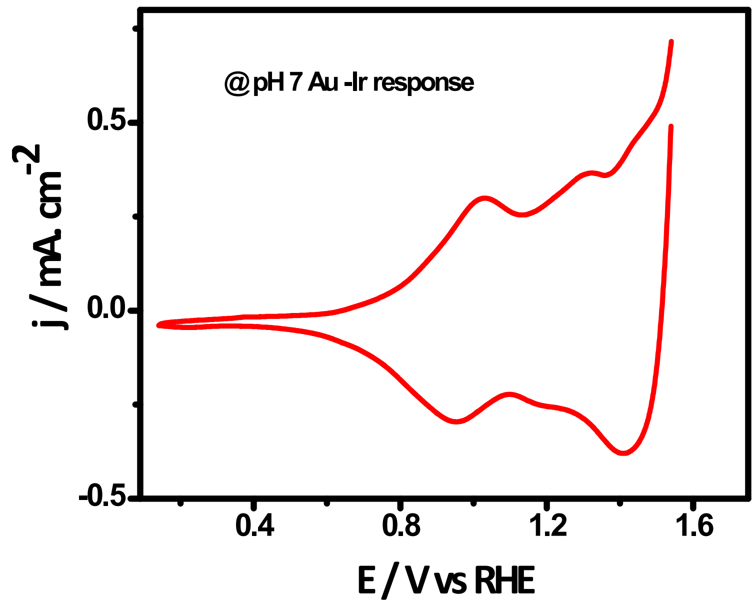


Figure S5. Cyclic voltammetric response of IrO$_x$ coated anodized Au in 0.5M phosphate buffer solution: pH 7; Scan rate: 0.05 V/s.

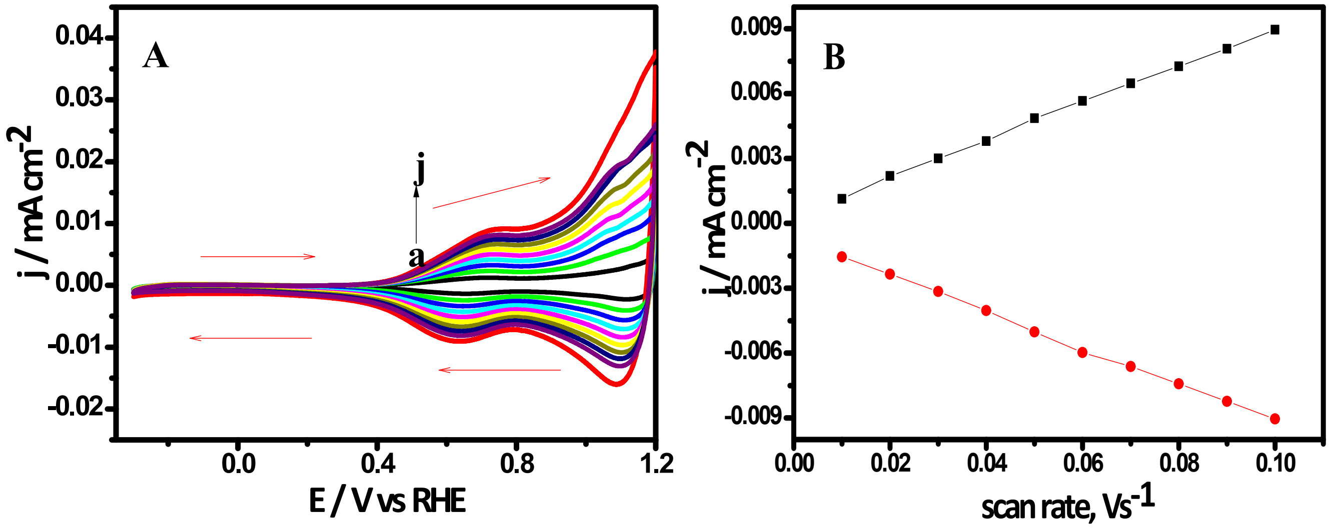


Figure S6. (a) Cyclic voltammetric response of the IrO$_x$ /Au electrode as a function of scan rate: **(A)** (a) 10 to (j) 100 mV/s in0.5M H$_2$SO$_4$; **(B)** Plot of peak current (*i*) vs. scan rate (ν)

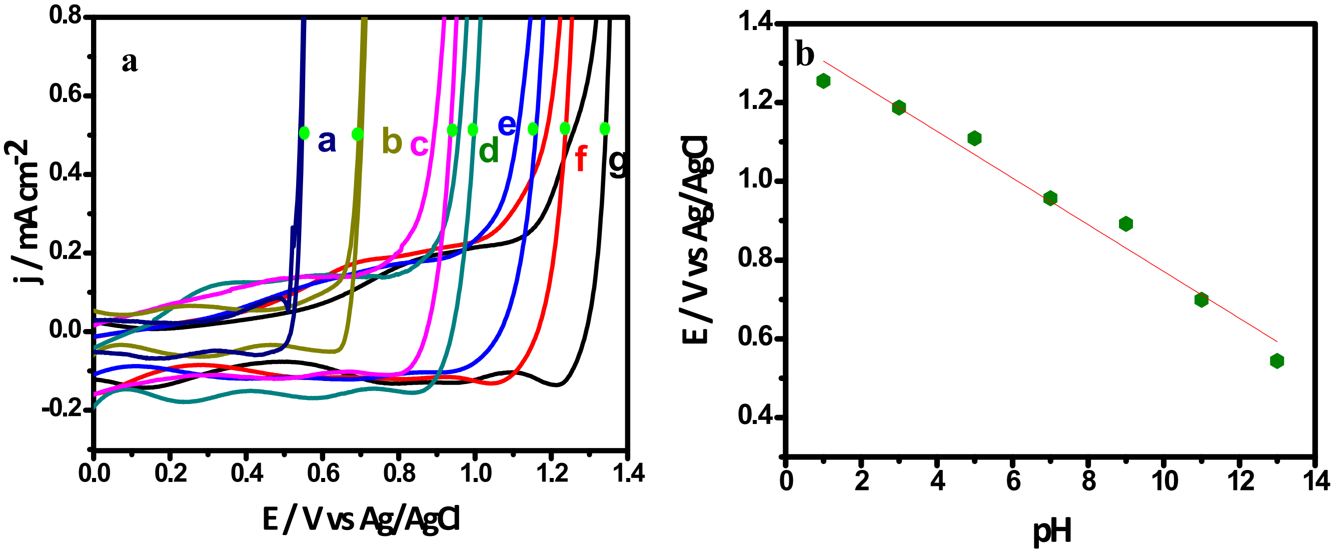


Figure S7. (A) Cyclic voltammetric responses showing the oxygen evolution reaction (OER) on Ir-coated anodized Au surface at pH values of: (a) 13; (b) 11; (c) 9.0; (d) 7.0; (e) 5.0; (f) 3.0; (g) 1.0; Scan rate = 0.05V/s. Electrolyte: 0.1M phosphate buffer. [Note: Green dots refer to the potential values where current is 0.5 mA.cm^{-2}]. (B) Plot of pH vs. OER at a current density of 0.5 mAcm^{-2}on Ir-coated anodized Au surface (Slope = -59.4 mV/decade). [Note: Refer to green dots in Figure A to locate the OER potentials].

Note:

Ag/AgCl reference electrode was used for two reasons: (a) it is not appropriate to use RHE and Hg/HgO for studies involving pH effect on the oxygen evolution reaction; and for this reason, (b) it is convenient to employ Ag/AgCl reference electrode with care exercised in avoiding chloride contamination with the use of a salt-bridge containing a non-halide electrolyte in the salt-bridge, as has been implemented in several publications, for example in ESI-Refs.[2-4].

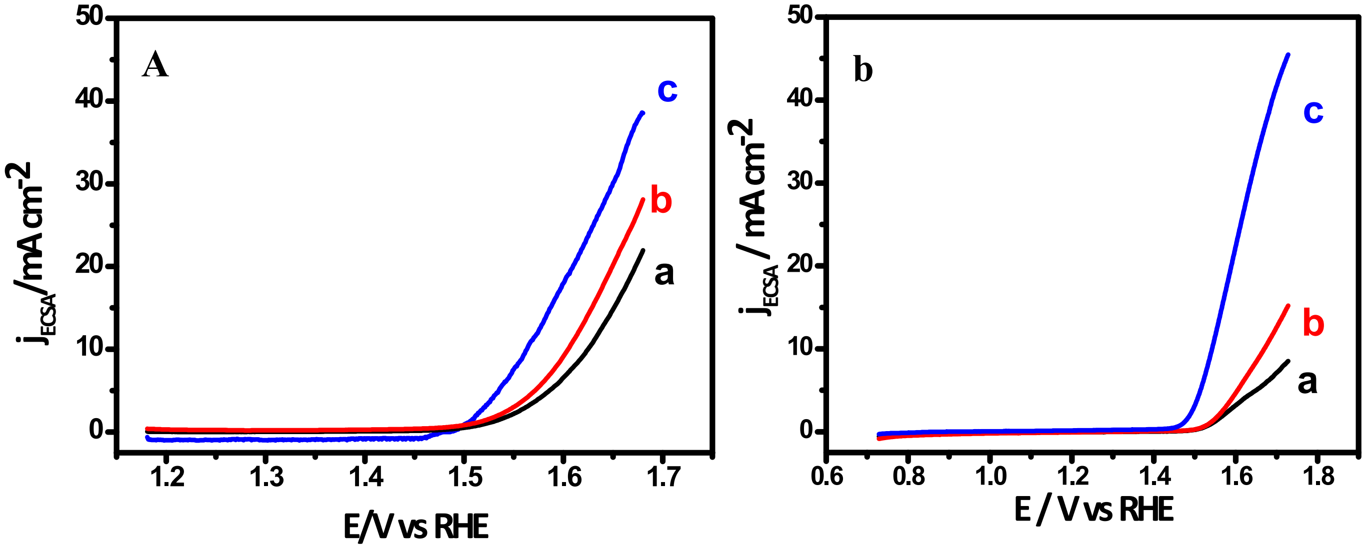


Figure S8. Linear sweep voltammetry showing oxygen evolution reaction on IrO_xcoated Au surface at a scan rate of 0.01V/s in **(A)** 0.5M H_2SO_4 and **(B)** 0.1 M NaOH solutions (a) IrO_x (electrochemically coated on GC), (b) *pc*-Ir surface; (c) IrO_x/anodized Au surface

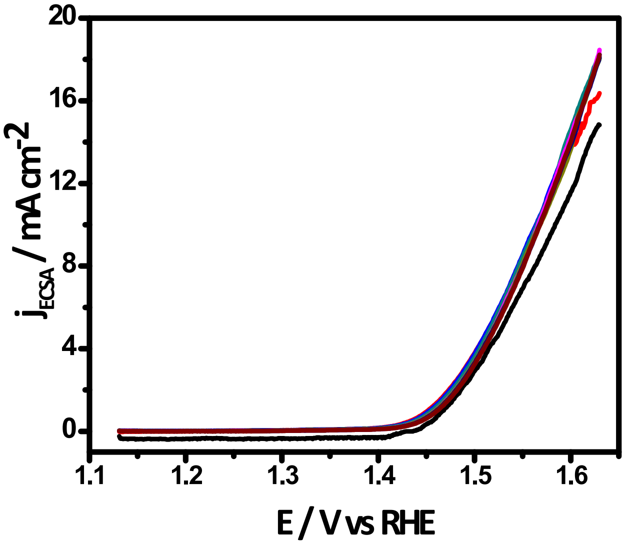


Figure S9. Linear sweep voltammetry of Ir coated (anodized) Au surface at a scan rate of 0.01V/s in 0.1 M NaOH [every 15th cycle shown (a) to (h) for a total of 120 cycles].

Note: See main text

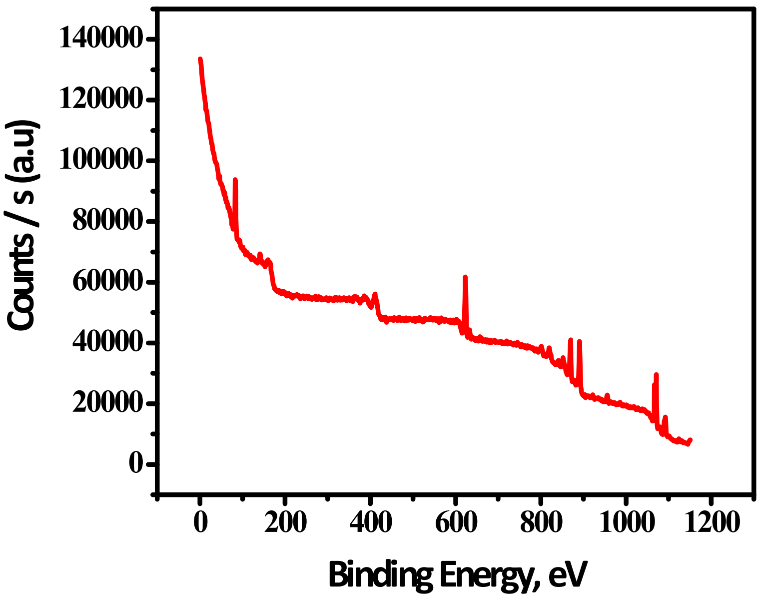


Figure S10. XPS data derived from analysis of an Ir-IrOx coated anodized Au surface.

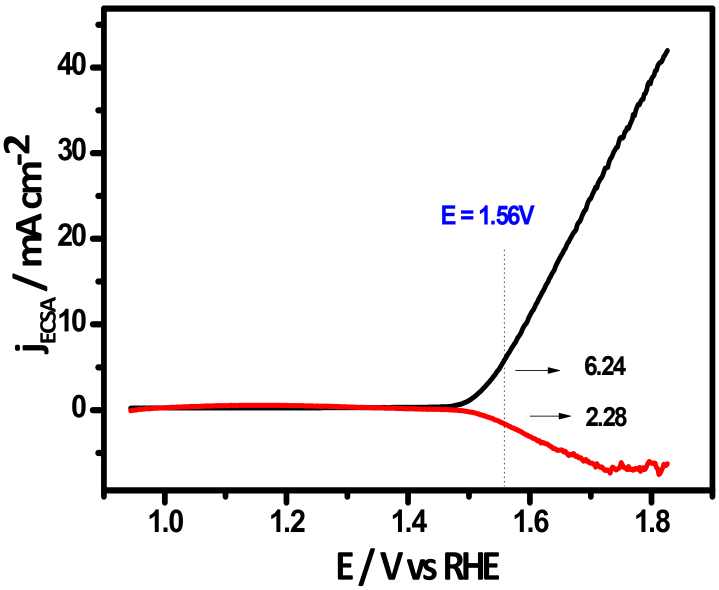


Figure S11(a) RRDE voltammetric data for

(a) OER reaction on Ir-coated anodized Au disk electrode at a scan rate of 0.01V/s in 0.1 M NaOH; and

(b) corresponding oxygen reduction reaction at the Pt ring electrode held at 0.5 V vs. RHE rotation at 1600 rpm.

Collection Efficiency (calculation)

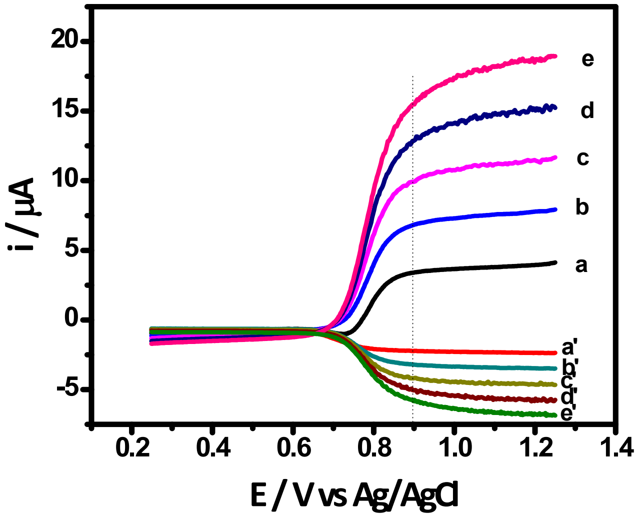


Figure S11(b) RRDE voltammetry of 1mM of $[Fe(CN)_6]^{3-}$ in 0.5M H_2SO_4 solution @ 0.02Vs^{-1} on 6 mm diameter Au disk Pt ring electrode. Notations (a)-(e) represent disk current and (a'-e'), the ring current for rotation rates of 100, 400, 900, 1600, 2500 rpm. The collection efficiency (N_{CL} of the ring electrode in the RRDE) is calculated by using the data from this figure). The calculated collection efficiency values at various rotation rates are tabulated below

S.No	Rotation rate (rpm)	Ring current (i_R, µA) @ 0.9V	Disk Current (i_D, µA) @0.9V	Collection Efficiency
1	100	2.0	5.1	0.38
2	400	3.7	9.6	0.36
3	900	4.4	12.8	0.37

4	1600	5.1	14.2	0.36
5	2500	5.8	15.5	0.39
Average (**collection efficiency**) = **0.372**				

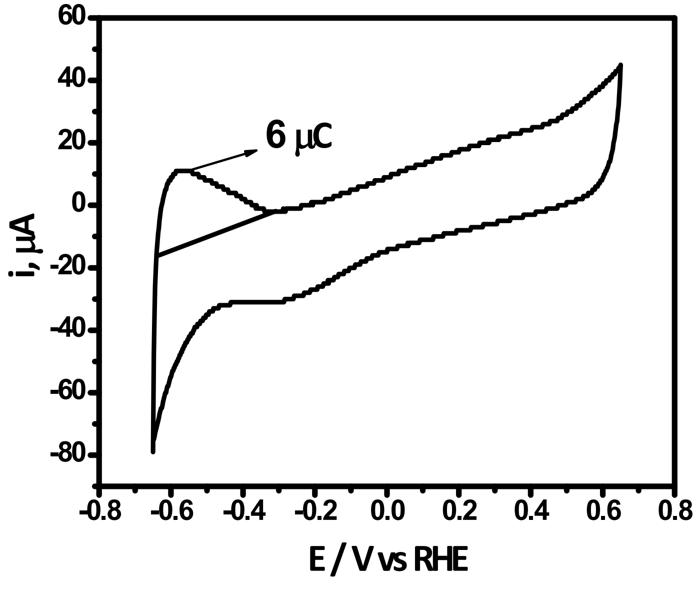


Figure S12. Voltammetric response of Pt ring in 0.5M H_2SO_4; Scan rate: 0.05Vs^{-1}

Calculation of iridium oxide concentration from RRDE experiments

In order to obtain all current values in terms of current density, ECSA was calculated for both (a) IrO_x-coated anodized Au disk surface; and (b) Pt ring surface using the charge under the hydrogen underpotential deposition peak recorded (a) on Ir coating (Fig.1C); and (b) on Pt disk surface (Fig.S12), respectively.

[1] H-UPD charge on 1 cm^2 iridium surface = 198μC [Ref.5]

[2] Charge under the cyclic voltammetric peak in Figure 1C = 129 μC cm^{-2}

The ratio, [2]/[1], i.e., 129/198 = 0.65 yields a value for ECSA for Ir-coated anodized Au surface. Using this ECSA value, we have converted current values into current density in the RRDE voltammograms.

[Note: Discernible H-upd peak responses were obtained at high scan rate values]. [One monolayer of Ir(111) contains $1.54*10^{15}$ atoms per cm^2, according to Ref.[6] mentioned below].

[This fractional monolayer coverage was also reported by V.I.Briss et al. in J. Mater. Chem., 2009, 19, 8244].

Ring surface:

H-UPD on platinum ring surface of $1cm^2$ geometrical surface area = 210 μC then ECSA of ring

Taking the real charge consumed, i.e., 6 μC, one may divide it by the theoretical value of 210 μC to obtain the ratio of 0.0285 for calculating ring current density [from Fig.S12].

Calculation of Turn-over frequency (TOF)

(a) From current at 1.56V

OER current at 1.56V = $6.24*10^{-3}$ $A.cm^{-2}$ [ECSA is used]

Number of Ir atoms = ca. 1.54 $*10^{15} cm^{-2}$ *(calculated based on the monolayer Ir(111)* Ref.[6]. This work formed the basis for the calculation of surface concentration of iridium).

TOF= $i*N_A / A*F*n*\Gamma$

where i = current

N_A= Avogadro number

A = Geometrical surface area of the electrode

F = Faraday constant

n = Number of electrons

Γ = Surface concentration

$\mathrm{TOF}_{\mathbf{1.56V}}$ = $[(6.24*10^{-3})(6.023*10^{23})] / [(1)(96485)(4)(1.54*10^{15})] = 6.3\ \mathrm{s}^{-1}$

Condition	Potential (V) vs. Ag/AgCl
Au in 0.1M NaOH	0.78
Anodized Au + 0. 1M NaOH	1.00
Anodized Au + 0.1M NaOH + $IrCl_3$	0.60
Anodized Au + 0.1M NaOH + $IrCl_3$ After 25 min	0.58
After 1 Hour	0.45

Table S1: Open circuit potential values

(b) From RRDE voltammetry (Disk potential held at 1.56V)

Turn-over frequency (TOF) = $i_R/N_{cl}rnAF$
i_R= ring current density (A cm^{-2}); N_{CL} = collection efficiency; r = Surface concentration (moles/cm^2); n = 4; A= ECSA, cm^2; F= Faraday's constant

$\mathrm{TOF}_{\mathbf{1.56V}}$ = $[2.28*10^{-3}]/[0.37*2.55*10^{-9}*4*1*96485]$

= $6.26\ \mathrm{s}^{-1}$

Table S2: Benchmarking IrO_x/Au (present work) against other IrO_x electrocatalysts [see references in this table]

Study No.	Iridium deposition method	TOF (s^{-1})	Method of calculation	Reference
1	Anodic deposition from homogeneous medium	8-11	RRDE-ring current at disc potential =1.98V vs RHE	R. W. Murray et al. *J.Am. Chem. Soc.* 2009, **131**,15578
2	By polyallylamine	6.36	OER-current at 0.28	Ho et al , *RSC Adv*,

	hydrochloride on GC		overpotential	**2**, 2012, 4092
3	SAM interaction between ITO and IrO_x colloids	6.66	OER- oxygen measurement (by Fluorescence probe)	M. Yagi et al. *J. Phys. Chem. Letts*, **109**, 2005, 21489
4	Electroflocculation	6.6	RRDE-ring current at disk potential =1.58 V vs RHE	R.W. Murray et al. *J. Phys.Chem C.*, **113**, 2009,12958
5	IrO_x/Au	6.3	OER-current at 1.56 V vs RHE	Present work
		6.26	RRDE- ring current at disk potential =1.56 V vs RHE	Present work

References

1) K. Nishio, H. Masuda, *Angew. Chem. Int. Ed.*, 2011, **123**, 1641.
2) T. Nakagawa, N.S. Bjorge, R.W. Murray, *J. Am. Chem. Soc.*, 2009, **131**, 15578.
3) Y. Zhao, E.A. Hernandez-Pagan, N.M. Vargas-Barbosa, J.L. Dysart, T.E. Mallouk, *J. Phys. Chem. Lett.*, 2011, **2**, 402.
4) T. Nakagawa, C.A. Beasley, R.W. Murray, *J. Phys. Chem. C.* 2009, **113**, 12958.
5) J. Durst, A. Siebel, C. Simon, F. Hasche, J. Herranz and H. A. Gasteiger, *Energy Environ. Sci.*, 2014, **7**, 2255.
6) S. Wehner, J. Cisternas, O. Descalzi, J. Kuppuers, *Eur. Phys. J.* Special Topics 2014, **223**, 21.