

Atomic Iridium@Cobalt Nanosheets for Dinuclear Tandem Water Oxidation

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Supporting Information

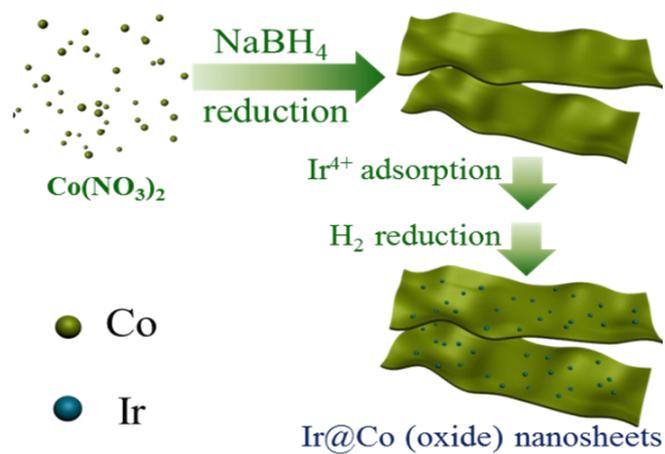


Figure S1 Schematic illustration of the synthesis of Ir@Co nanosheets.

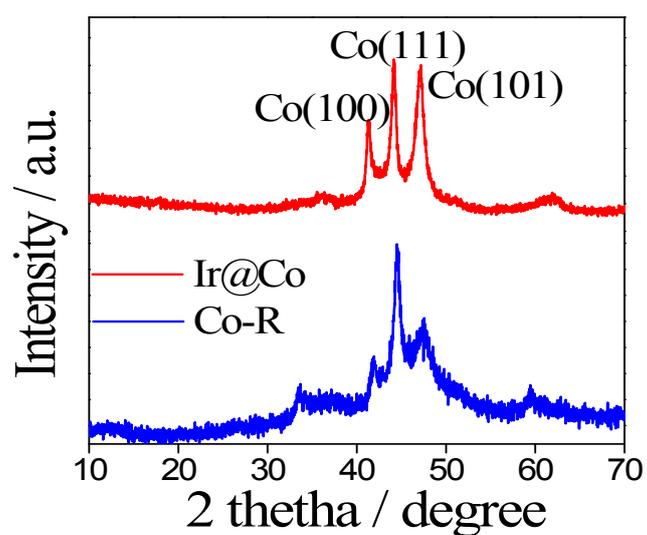


Figure S2 XRD patterns of Co-R and Ir@Co.

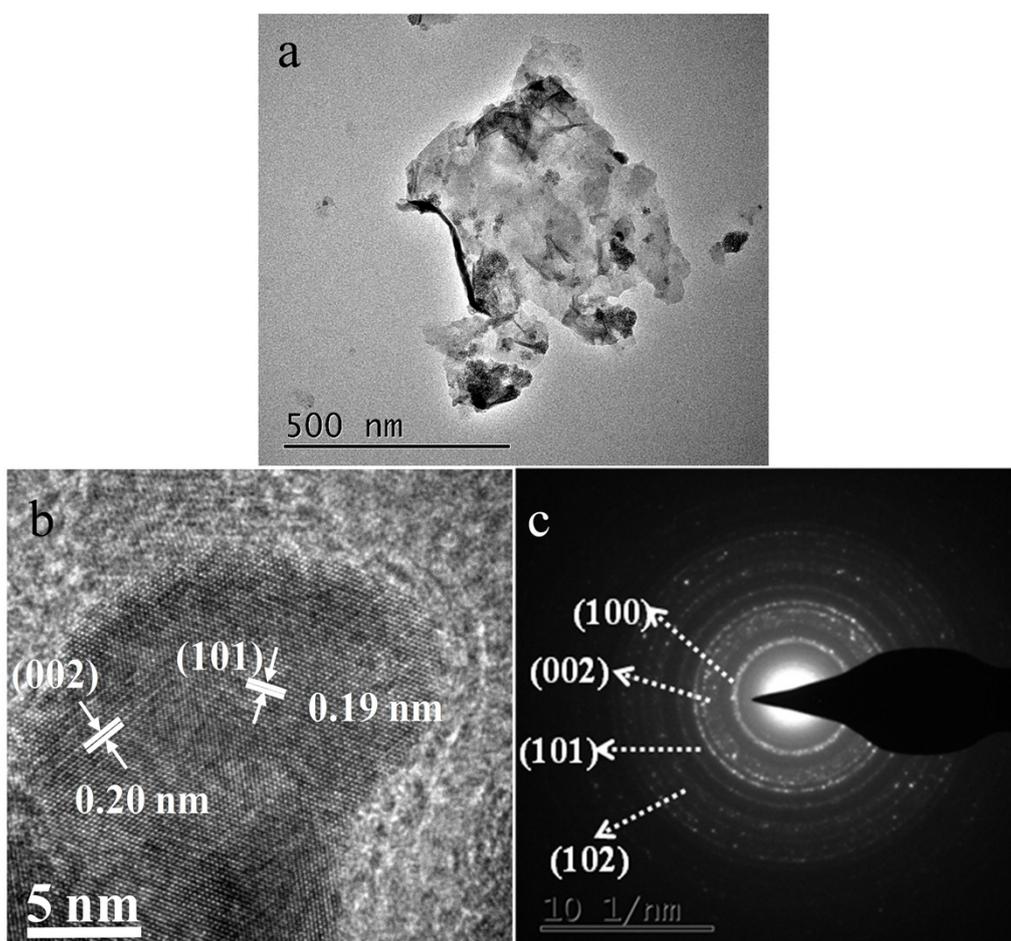


Figure S3 (a,b) Low- and high-magnification transmission electron microscopy (TEM) images and (c) selected area electron diffraction (SAED) of Ir@Co nanosheets.

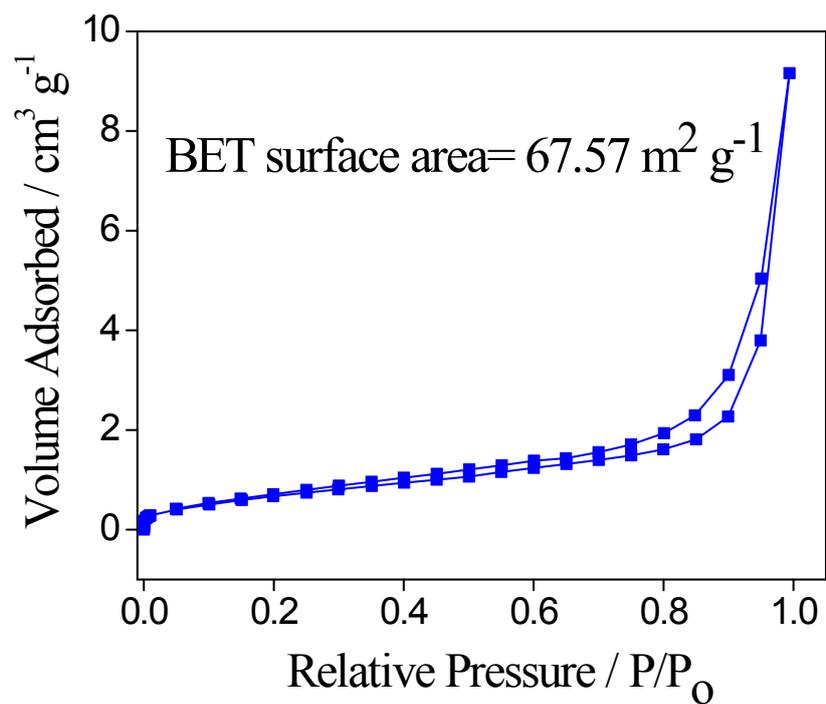


Figure S4 N₂ adsorption-desorption isotherm of the 2D Ir@Co nanosheets for determination of the Brunauer–Emmett–Teller (BET) surface area.

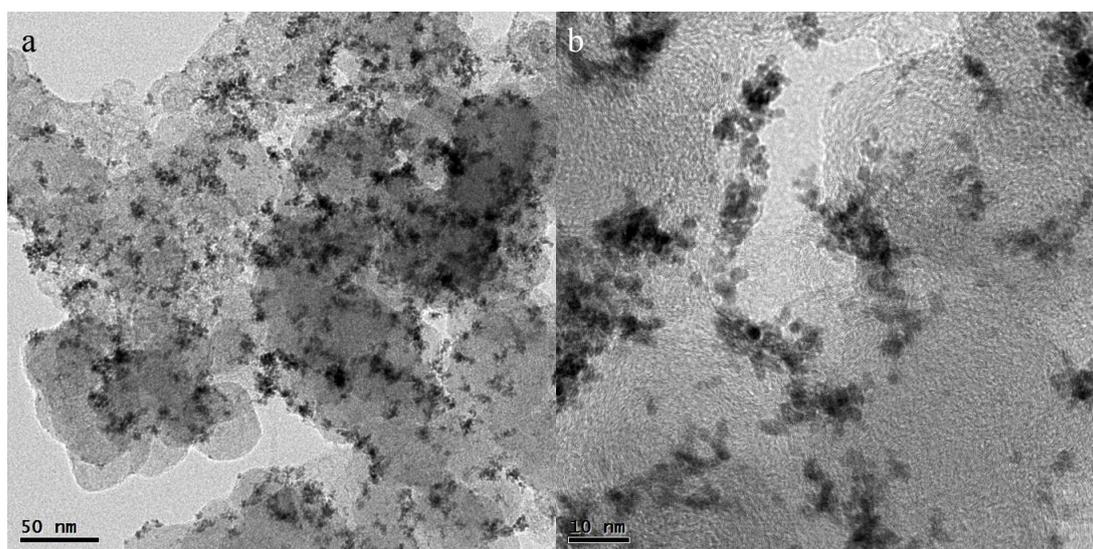


Figure S5 (a,b) Low- and high-magnification TEM images of Ir/C material.

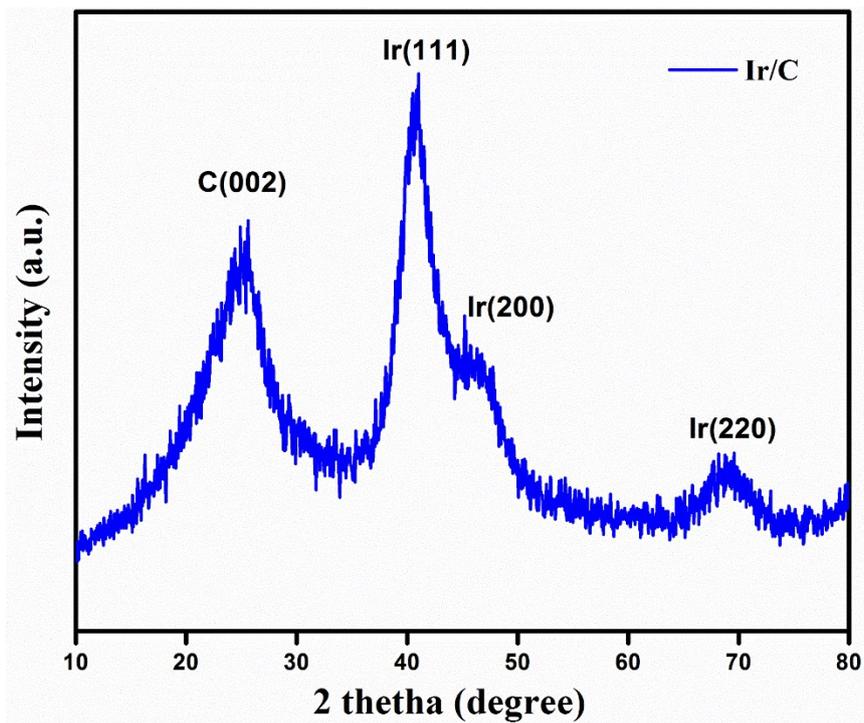


Figure S6 X-Ray Powder Diffraction of Ir/C.

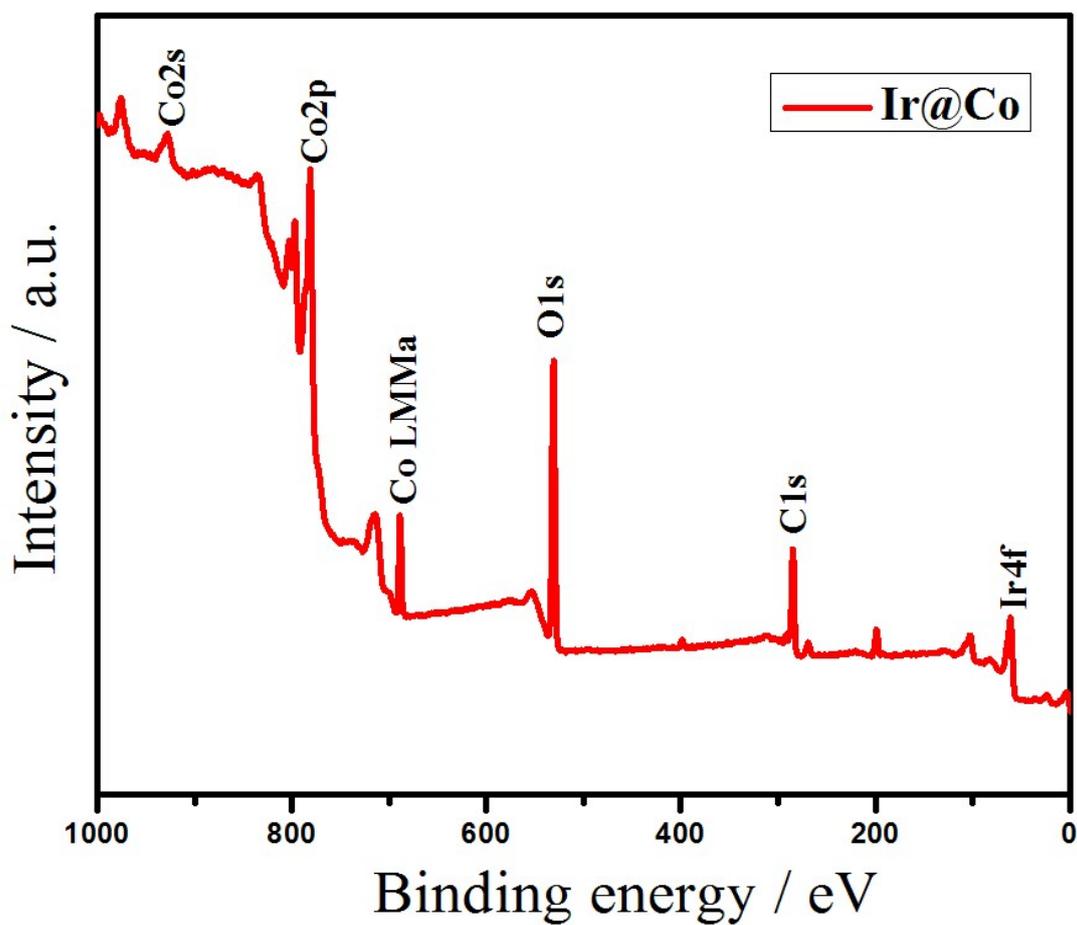


Figure S7 The survey XPS spectrum of Ir@Co.

Table S1. Contents of O1~O4 in the materials as determined by XPS analysis.

	Ir@Co (at.%)	Co-A(at.%)	Co-R (at.%)
O1	1.7	24.1	4.4
O2	18.3	39.5	28.1
O3	33.1	25.3	25.1
O4	46.9	11.2	32.4

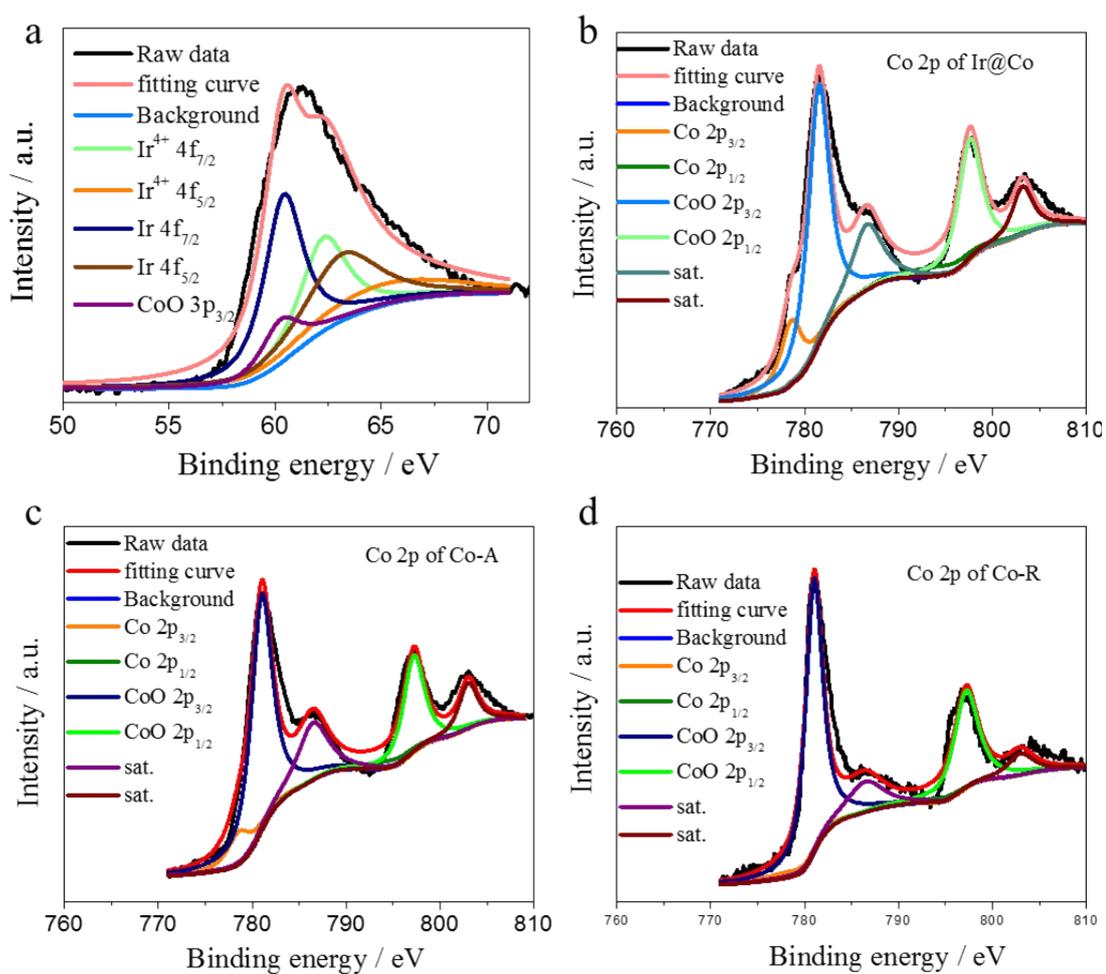


Figure S8 High-magnification XPS spectra in (a) Ir 4f region of Ir@Co, (b) Co 2p region of Ir@Co, (c) Co 2p region of Co-A and (d) Co 2p region of Co-R.

Table S2 Fitting parameters of EXAFS data.

Sample	Ir-Co		D. W.	ΔE_0 (eV)
	R (\AA)	CN		
Ir@Co	2.55 ± 0.01	8.8 ± 1.2	0.005 ± 0.001	8.4 ± 2.1

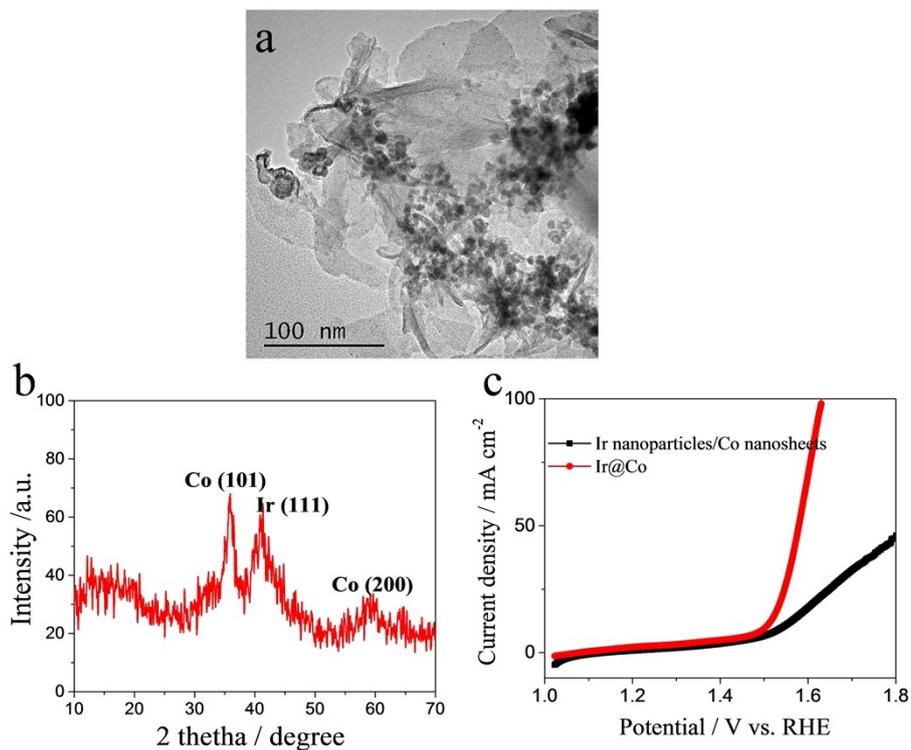


Figure S9 (a) TEM image of Ir nanoparticles/Co nanosheets. (b) XRD of Ir nanoparticles/Co nanosheets. (c) LSV curves for Ir@Co and Ir nanoparticles/Co nanosheets.

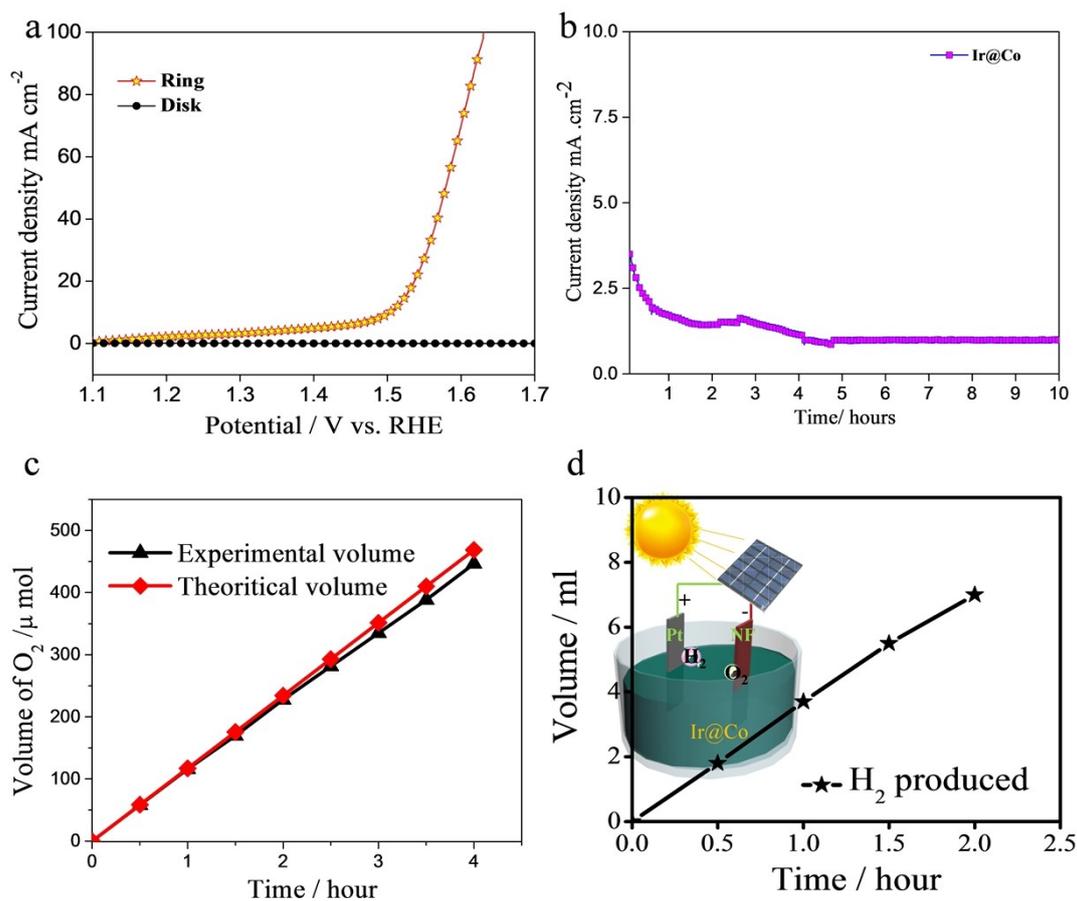


Figure S10 (a) Rotating ring-disk electrode (RRDE) test of Ir@Co in 1 M KOH solution with IR corrections; (b) chronoamperometry test of Ir@Co sample; (c) O_2 production volumes as a function of water-oxidation time. (d) Hydrogen production along with electrolysis time by solar cell-driven overall water splitting, using a commercial planar polycrystalline Si solar cell and a Pt plate as the counter electrode.

Table S3 Comparison in OER performance of some noble metal-based catalysts reported recently in literature.

Source/References	Solution	Loading	Tafel slope value mV dec ⁻¹	Overpotential at 10 mA cm ⁻² (mV)
<i>This work (Ir@Co)</i>	1 M KOH	0.0034 mg_{Ir} cm⁻²	99	273
<i>J. Am. Chem. Soc.</i> , 2015, 137, 13031–13040 (Ir-Ni oxide)	0.1 M HClO ₄	-	-	305
<i>Angew. Chem. Int. Ed.</i> , 2016, 55, 742–746 (IrO _x -Ir)	0.5 M H ₂ SO ₄	1 mg _{Ir} cm ⁻²	43.7–44.7	295
<i>Angew. Chem. Int. Ed.</i> , 2015, 54, 2975–2979. (IrNiO _x)	0.05 M H ₂ SO ₄	0.01 mg _{Ir} cm ⁻²	-	280
<i>Science</i> , 2016, 353, 1011-1014. (IrO _x /SrIrO ₃)	0.5 M H ₂ SO ₄	Pure SrIrO ₃ film electrode	-	270-290
<i>Chem. Sci.</i> , 2015, 6, 3321-3328 (Irnanodendrites)	0.05 M H ₂ SO ₄	0.01 mg _{Ir} cm ⁻²	55.6-57.0	280
<i>Nano Lett.</i> , 2016, 16, 4424–4430 (Ultrathin Laminar Ir)	1 M KOH	0.01 mg _{Ir} cm ⁻²	32.7	242
<i>Adv. Mater.</i> 2017, 29, . https://doi.org/10.1002/adma.201703798 (IrCoNi)	0.1 M HClO ₄	0.01 mg _{Ir} cm ⁻²	53.8	303
<i>Adv. Mater. Interfaces</i> 2018, 1800392 (Co/N-CNTs@Ti ₃ C ₂ T)	0.1 M KOH	0.408 mg cm ⁻²	79.1	410
<i>Advanced Materials</i> , 2017, 29, 1606793 (Fe ₁ Co ₁ -ONS)	0.1 M KOH	0.36 mg cm ⁻²	36.8	308
<i>Adv. Funct. Mater.</i> 2017, 27, 1606497 (PPy/FeTCPP/Co)	0.1 M KOH	0.3 mg cm ⁻²	61	340
<i>Advanced Science</i> , 2018, 5, 1801029 (2D cobalt-based ZIF-9(III) nanosheets)	1 M KOH	0.21 mg cm ⁻²	55	380

Note: -represents not mentioned in the literature. All the potentials are calibrated and converted to reversible hydrogen electrode.

For Faradic efficiency calculation

Water splitting Potential: 2.0 V

Table S3. H₂ production and current change along with electrolysis time in solar-assisted water oxidation on Ir@Co nanosheet electrode.

Time / h	H ₂ / ml	Current / mA	Potential / V
0.5	2.4	10.2	
1	3.95	9.6	
1.5	5.5	8.6	
2	7.0	6.4	
Average		8.7	2.0

H₂ in practice: $0.007 \text{ L} / 22.4 \text{ L/mol} = 3.125 * 10^{-4} \text{ mol H}_2$

H₂ in theory: $(8.7 * 10^{-3} \text{ A} * 7200 \text{ s}) / 96500 * 2 = 104850 * 10^{-3} / 193000 \text{ mol} = 3.24 * 10^{-4} \text{ mol H}_2$

Faradic Efficiency = $3.125 * 10^{-4} / 3.24 * 10^{-4} = 96.4 \%$

For solar to hydrogen efficiency

Energy of solar: $0.00145 \text{ m}^2 * 1000 \text{ W/m}^2 * 7200 \text{ s} = 10440 \text{ W}$

Energy from H₂: $U * I * 7200 \text{ s} * \text{Faradic Efficiency} = 2.0 \text{ V} * 8.7 * 10^{-3} * 7200 \text{ s} * 0.964 = 124.3$

Solar to hydrogen efficiency = $124.3 / 10440 = 0.0119$ or 1.19 %

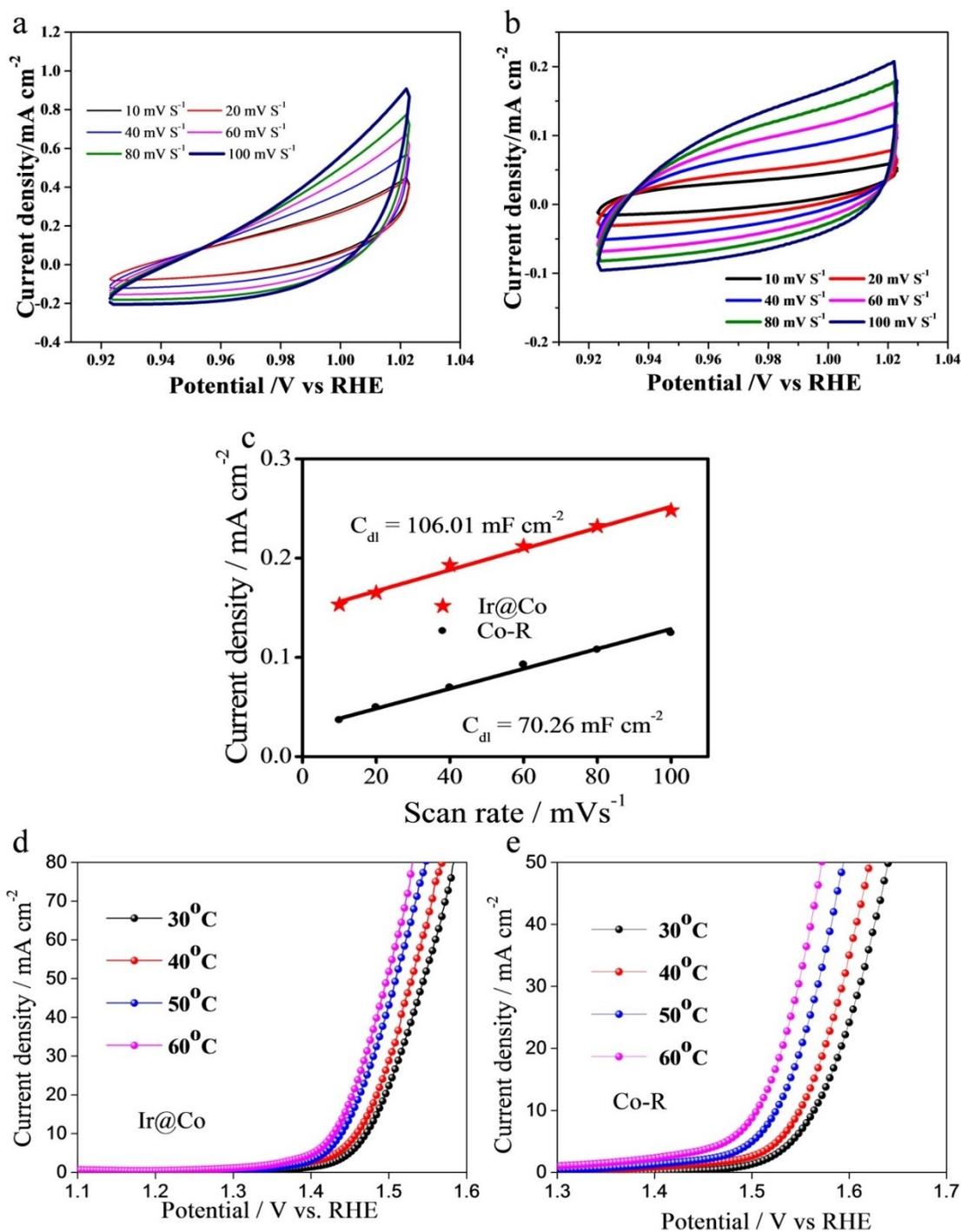


Figure S11 CVs of (a) Ir@Co and (b) Co-R measured in a non-Faradaic region at scan rate of 10 mV s⁻¹, 20 mV s⁻¹, 40 mV s⁻¹, 60 mV s⁻¹, 80 mV s⁻¹, and 100 mV s⁻¹, for determining the electrochemical active surface area of Ir@Co nanosheets and Co-R. (c) Electrochemical double-layer capacitance measurements (currents measured at 0.1 V vs. RHE as a function of scan rate) for Ir@Co and Co-R. (d and e) LSV curves for OER at different temperature.

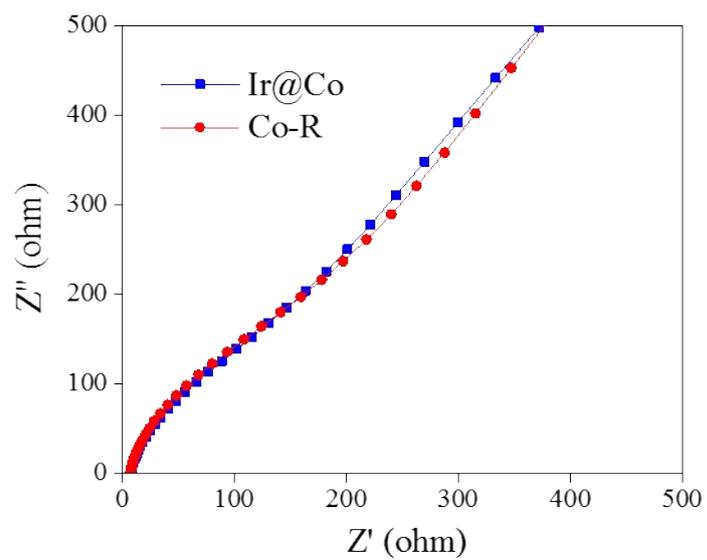


Figure S12 Electrochemical impedance spectroscopies (EISs) of Ir@Co nanosheet and Co-R.

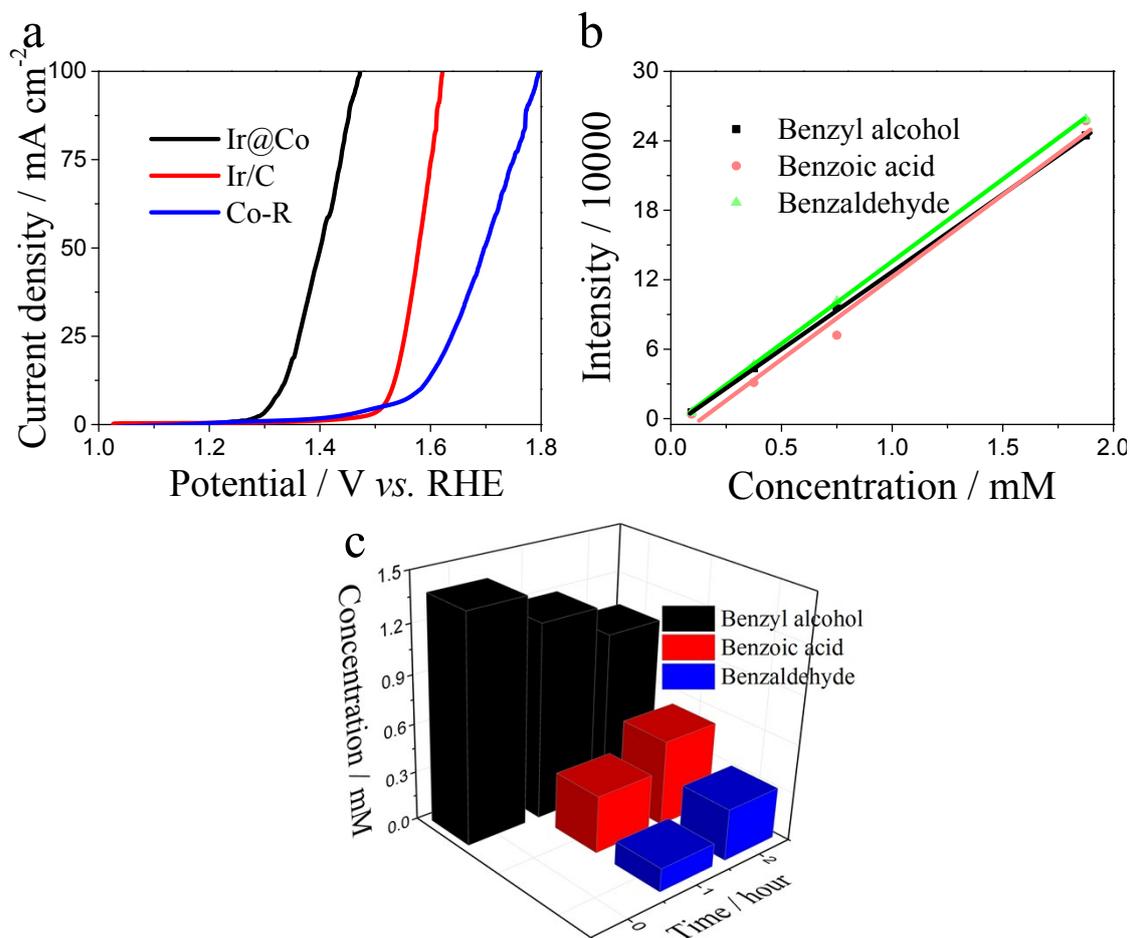


Figure S13 (a) LSV curves in 1 M KOH with 12.5 mM benzyl alcohol (BA) on the catalysts; and (b) standard curves for benzyl alcohol, benzaldehyde and benzoic acid. (c) shows the amount of benzyl alcohol, benzaldehyde and benzoic acid at 0, 1 and 2 hours.

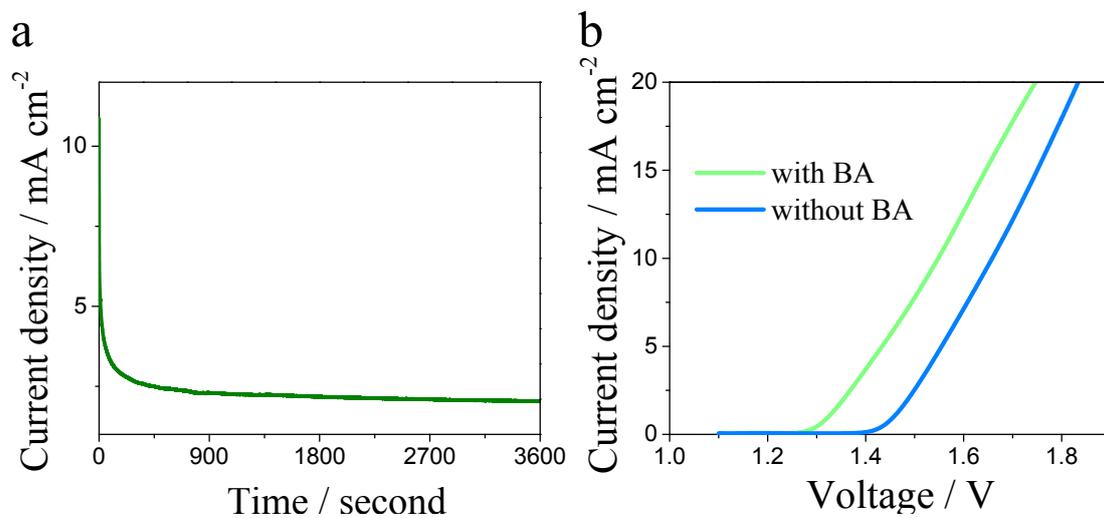


Figure S14 (a) Current-time curve at -0.5 V on Ir@Co material; (b) water splitting with and without BA.

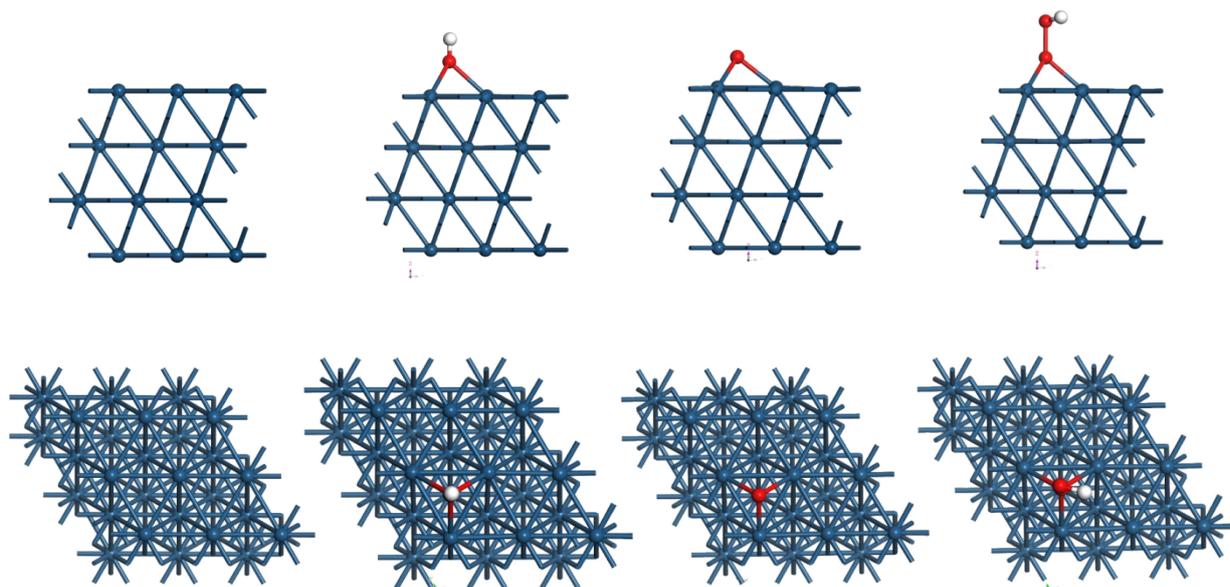


Figure S15 The OER processes on Ir/C model.