Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Fabricating Nano-IrO_2@amorphous Ir-MOFs Composites for Efficient Overall Water Splitting: One-pot Solvothermal Approach

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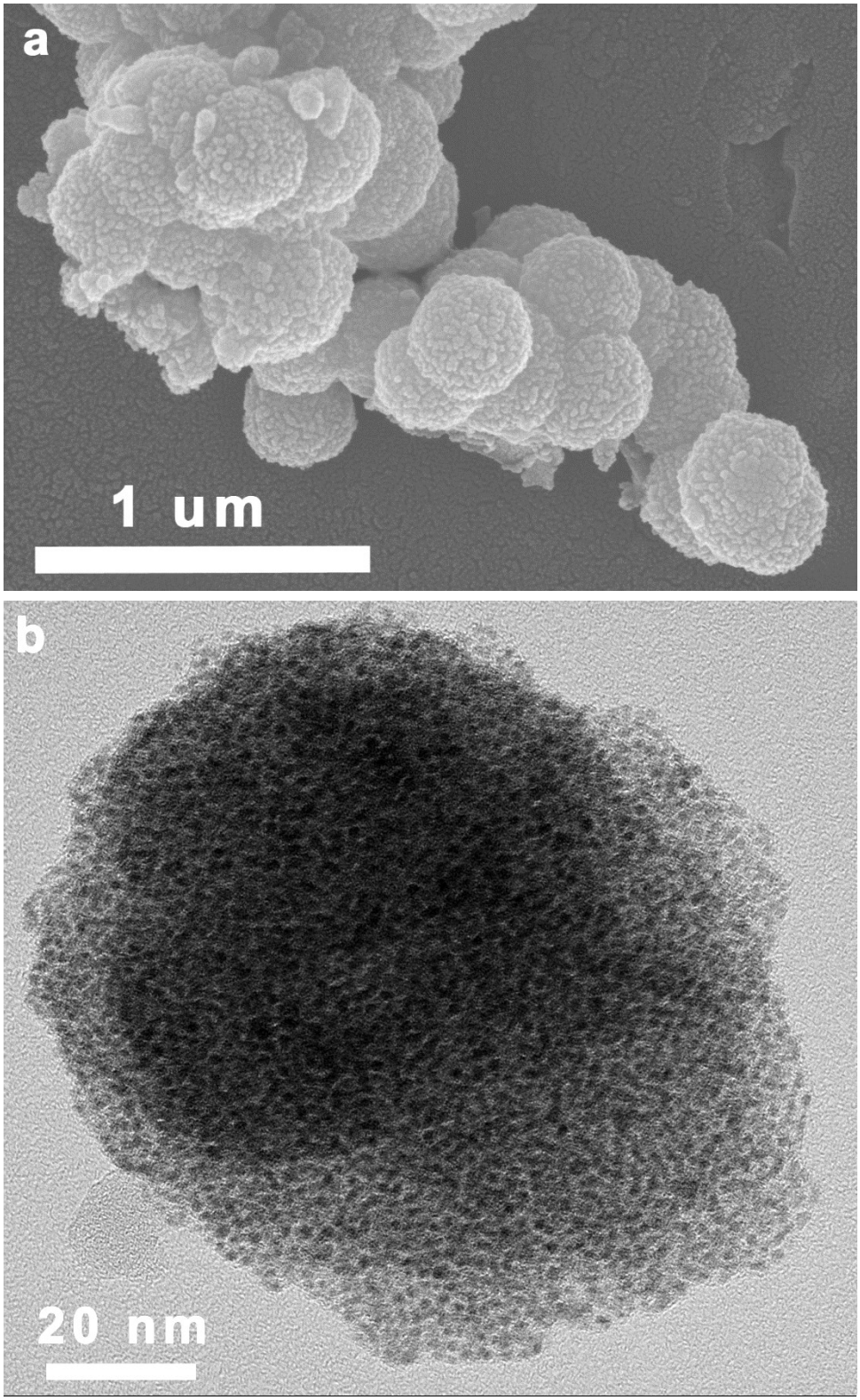


Figure S1. SEM (a) and TEM (b) images of IrO_2@Ir-MOF.

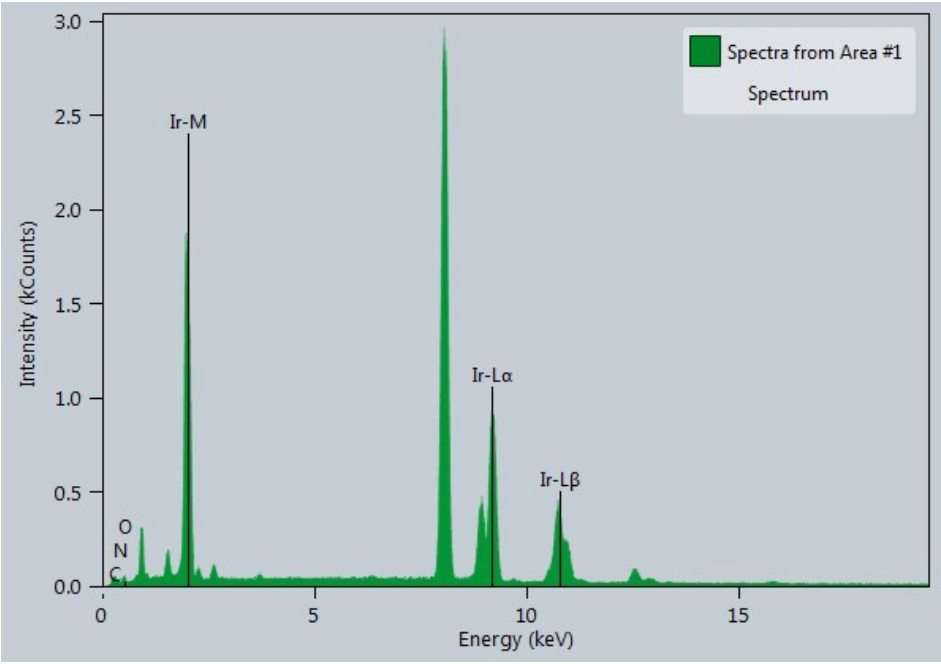


Figure S2. EDX of IrO_2@Ir-MOF.

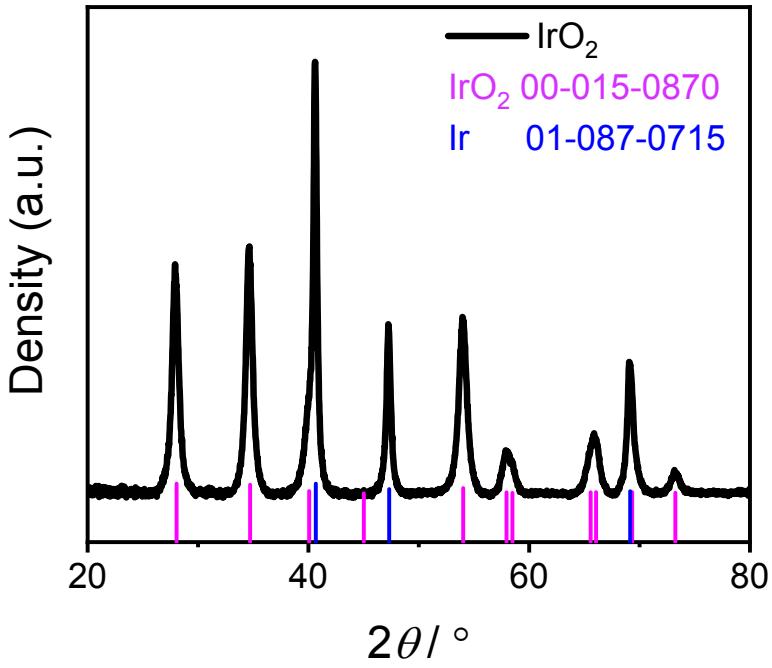


Figure S3. PXRD spectra of IrO_2.

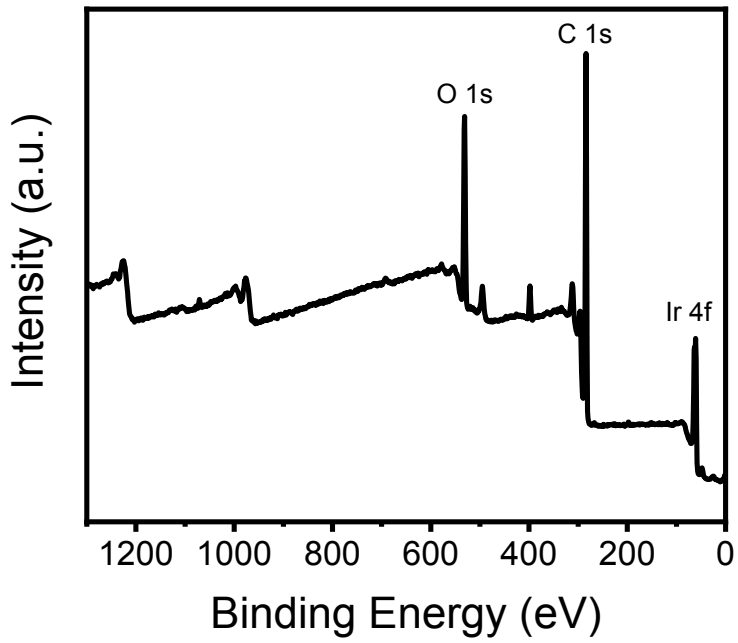


Figure S4. XPS spectra of IrO_2@Ir-MOF.

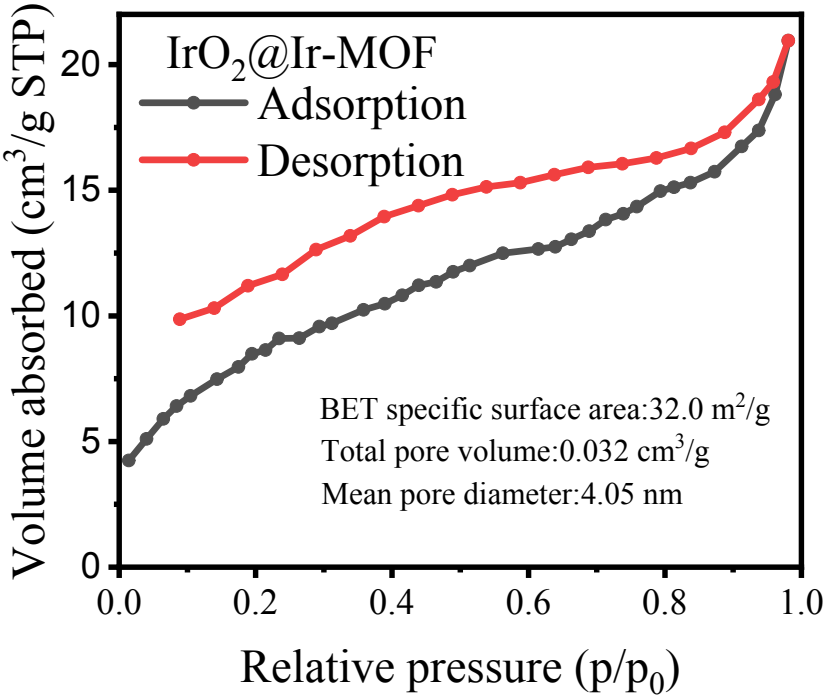


Figure S5. N_2 sorption isotherms of IrO_2@Ir-MOF at 77k.

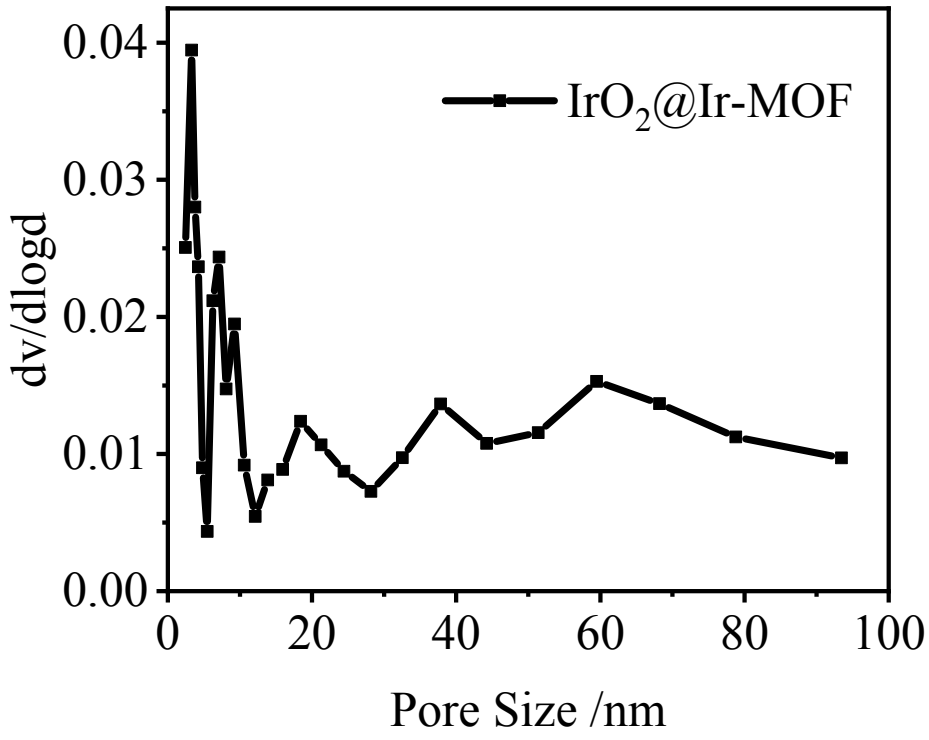


Figure S6. The corresponding mesoporous size distribution (BJH method) of IrO_2@Ir-MOF.

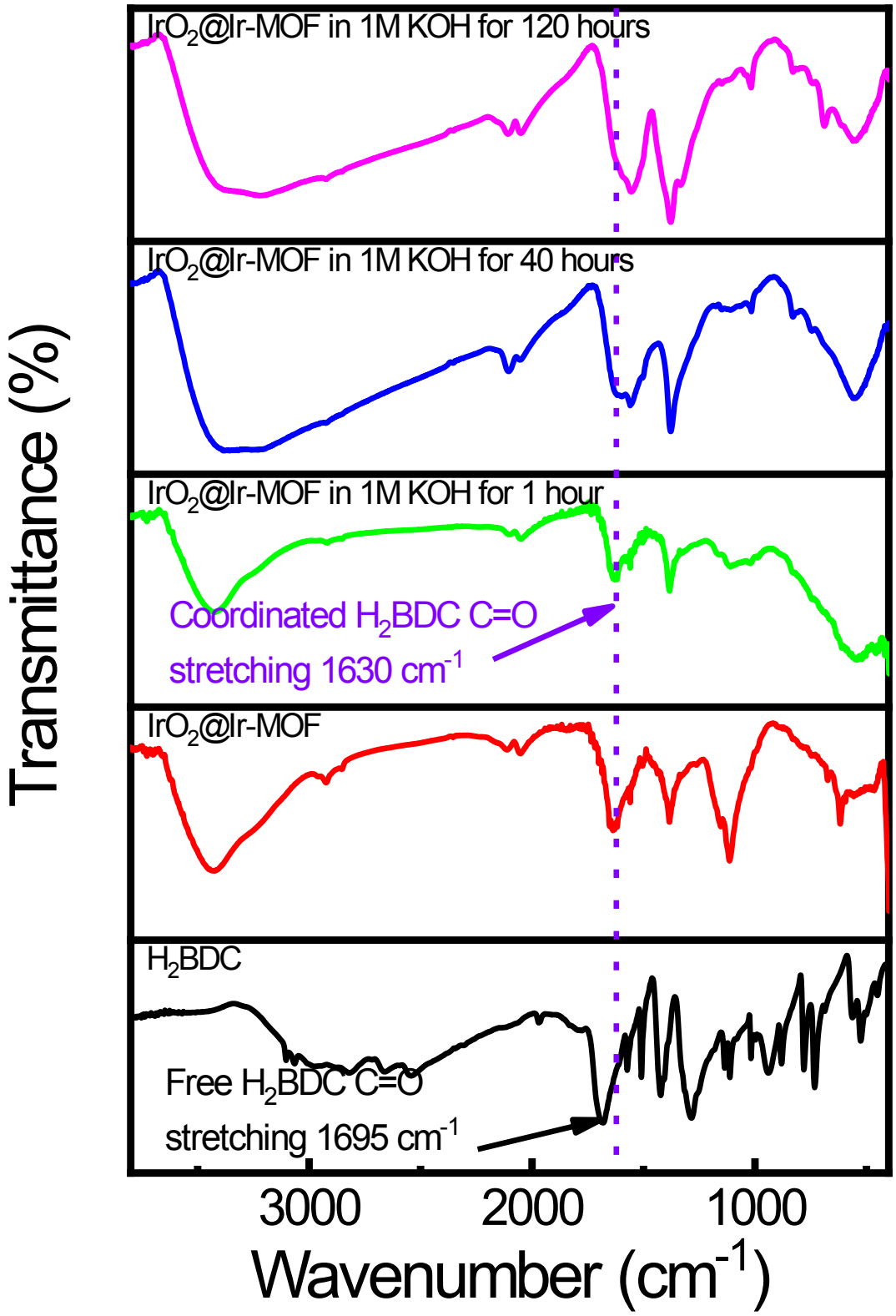


Figure S7. FTIR spectra of IrO_2@Ir-MOF and H_2BDC.

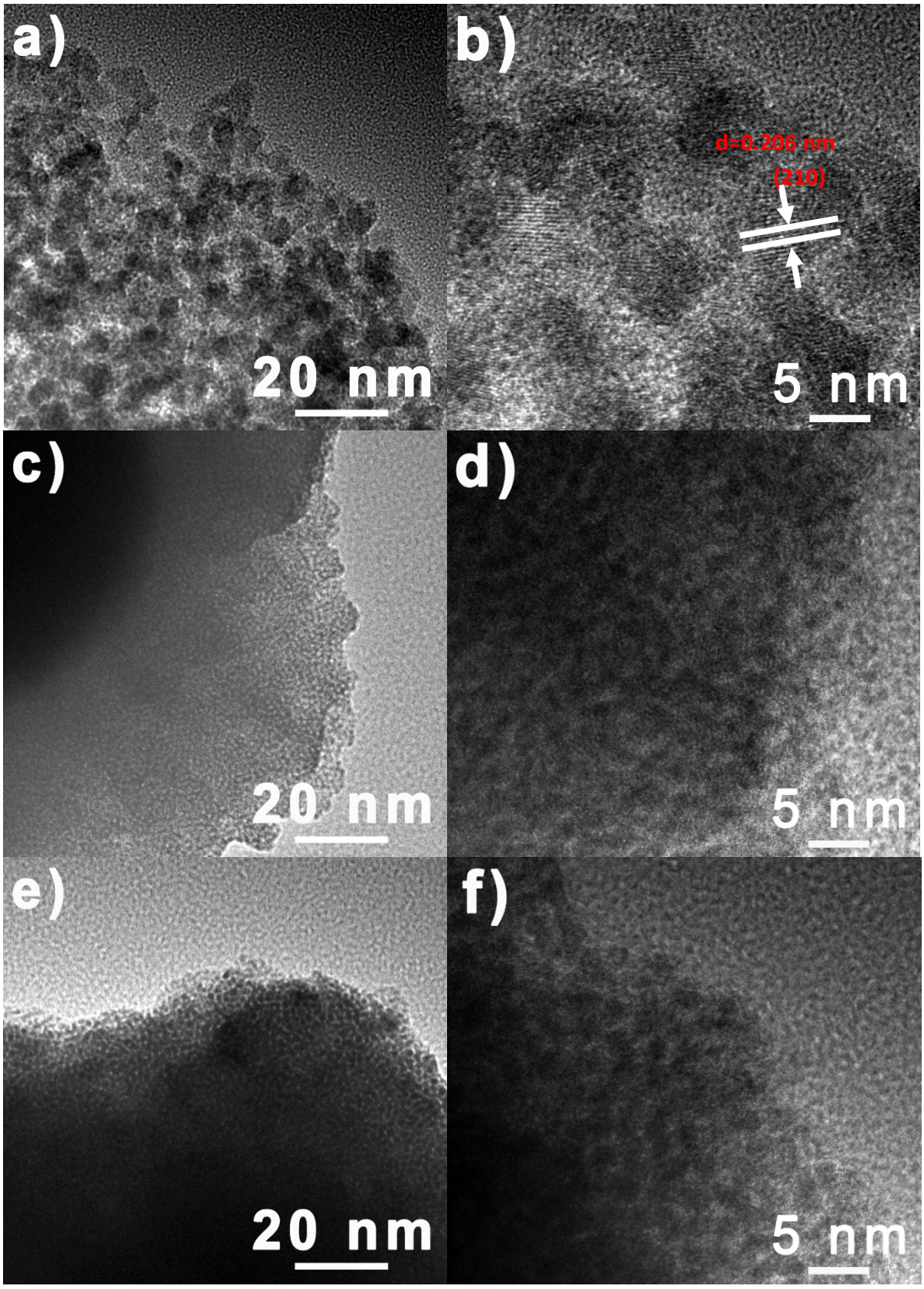


Figure S8. TEM images of IrO_2@Ir-MOF soaked in 1 M KOH solution for 1 (a, b), 40 (c, d) and 120 (e, f) hours.

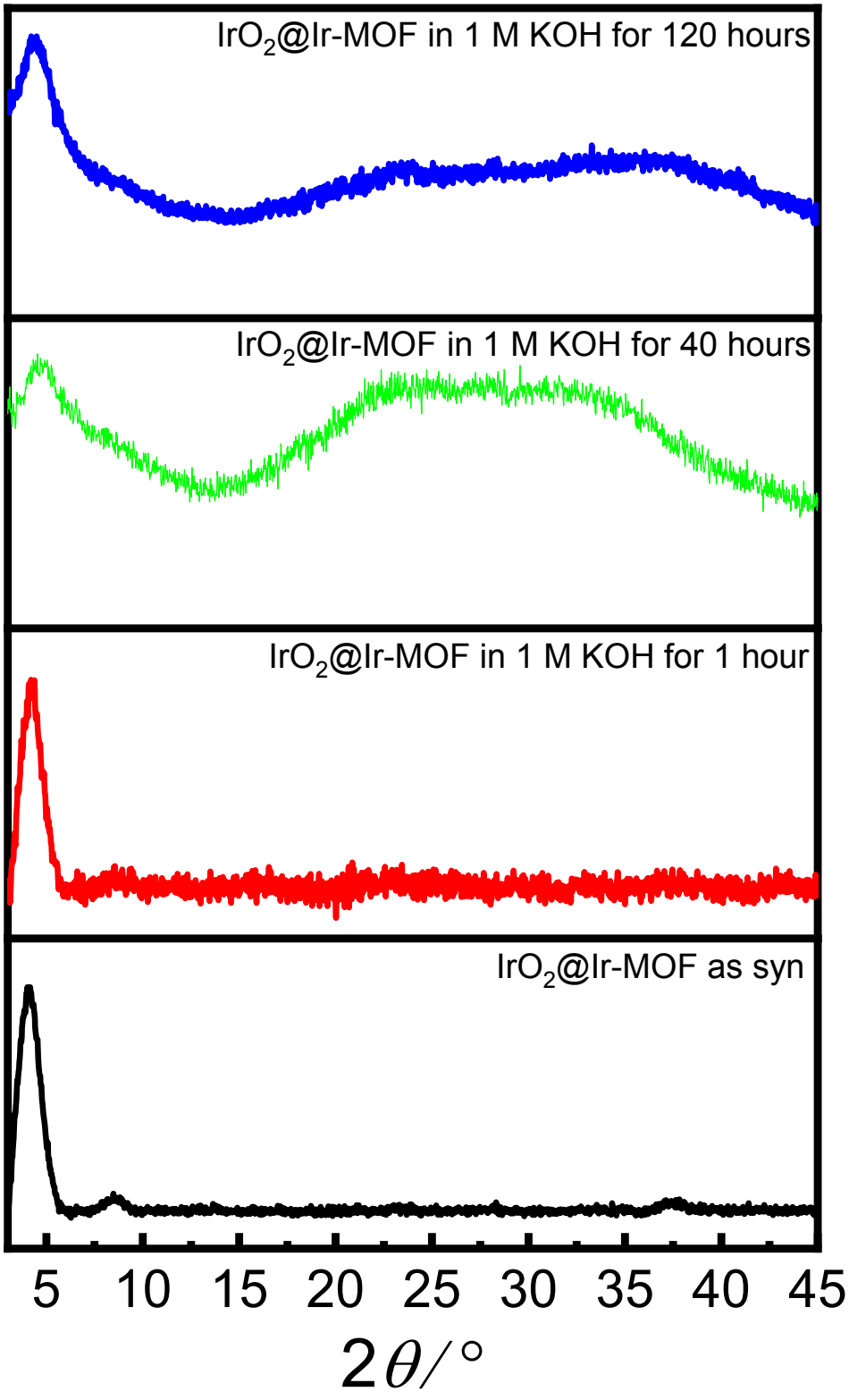


Figure S9. XRD patterns of as prepared IrO_2@Ir-MOF and soaked in 1 M KOH.

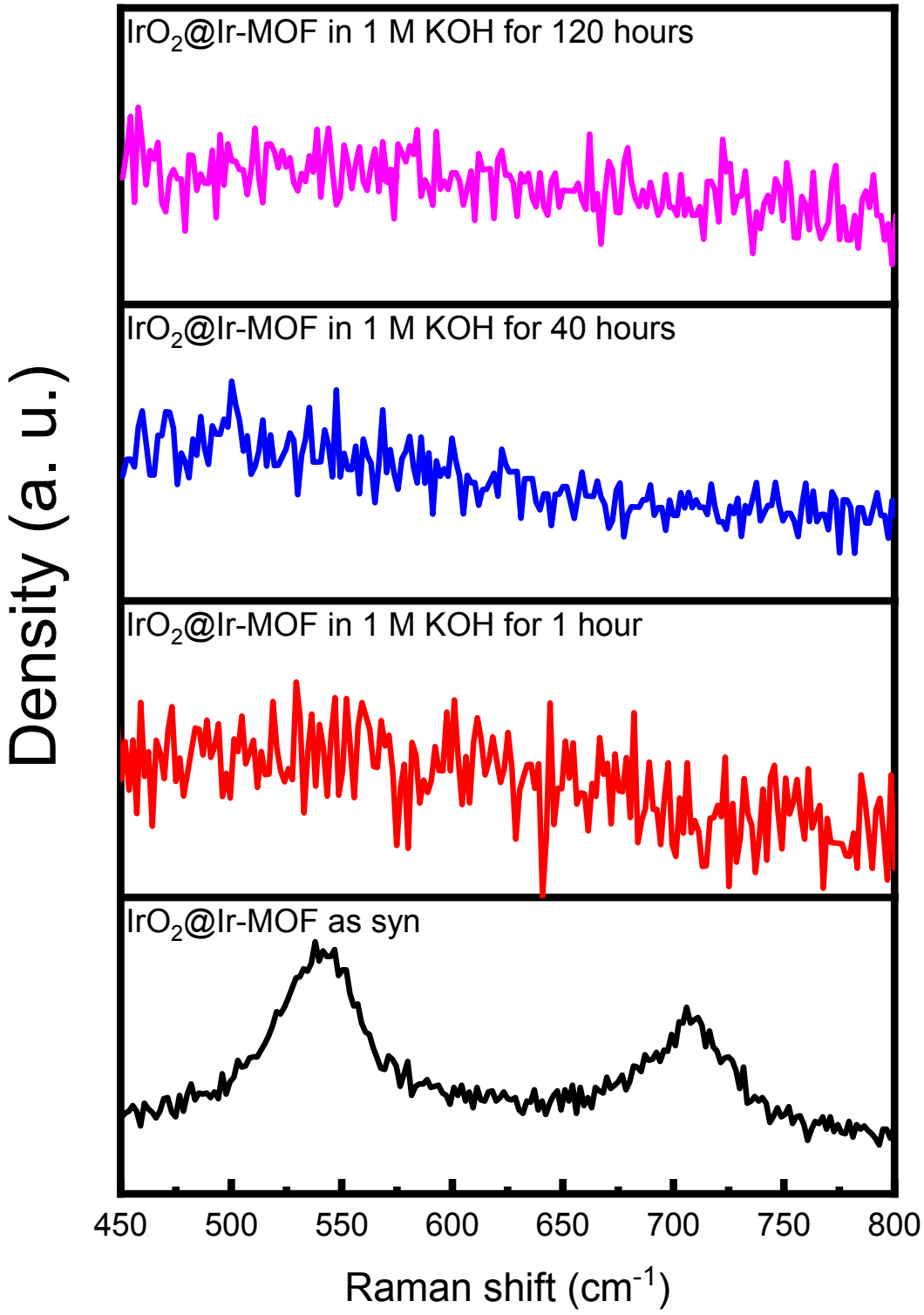


Figure S10. Raman spectra of as prepared IrO_2@Ir-MOF and soaked in 1 M KOH.

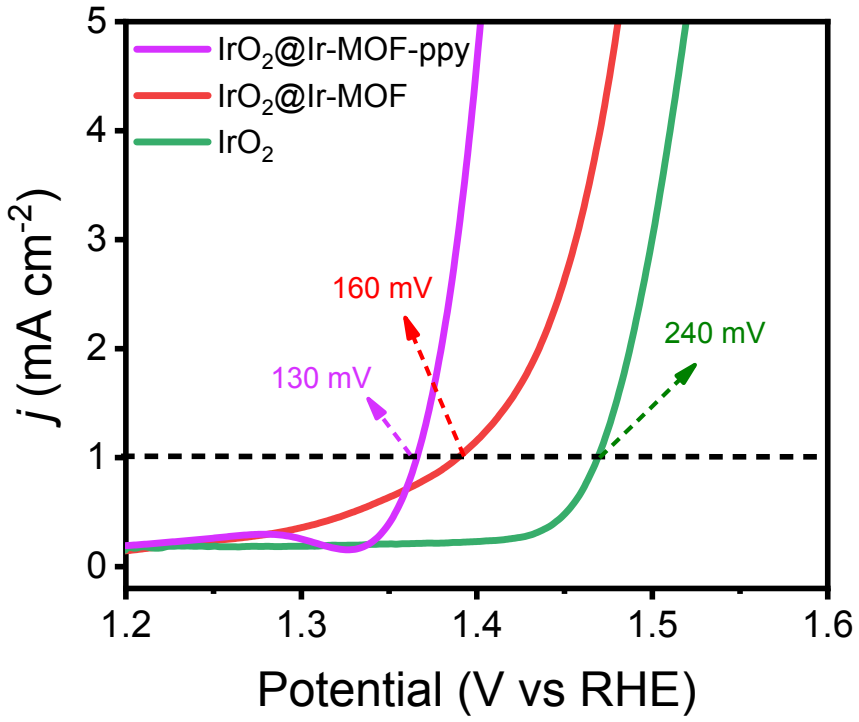
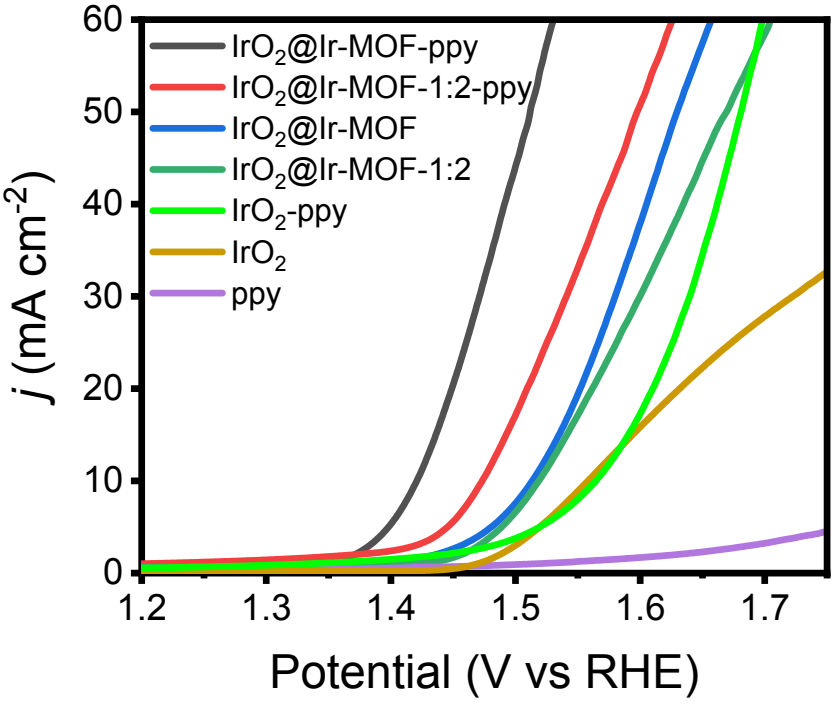


Figure S11. OER polarization curves.



Figures S12. Linear sweep voltammetry curves toward OER.

Table S1. Comparison of the OER activity of Ir-based catalysts in 1 M KOH electrolytes.

Catalyst	Overpotential (η_{10},mV)
IrO_2@Ir-MOF-ppy	207
IrO_2@Ir-MOF-1:2-ppy	244
IrO_2@Ir-MOF	284
IrO_2@Ir-MOF-1:2	289
IrO_2-ppy	332
IrO_2	328
ppy	---

Table S2. Summary of the recently reported OER electrocatalysts in 1 M KOH electrolytes.

Catalyst	**η_{10} /mV**	**Catalyst Loading /mg cm^{-2}**	**Ref**
IrO_2@Ir-MOF	207	20.4 μg_{Ir} cm^{-2}	This work
IrO_2/CC	209	35.5 μg_{Ir} cm^{-2}	*Adv. Energy Mater.* **2020**, 2001600
Ir NWs	224	None	*Adv. Funct. Mater.* **2018**, 28, 1803722
RuCu NSs/C-350 °C	234	None	*Angew. Chem. Int. Ed.* **2019**, 58, 2-8
IrO_2 (1:100)-450 °C	276	0.379 μg_{IrO2} cm^{-2}	*Nanoscale*, **2017**, 9, 9291-9298

Table S3. The Ir loading of electrodes based on different catalysts calculated from ICP-OES.

Catalysts	**Ir loading（ug cm^{-2}）**
IrO_2@Ir-MOF-ppy	20.4
IrO_2@Ir-MOF	20.4
ppy	None
IrO_2	80

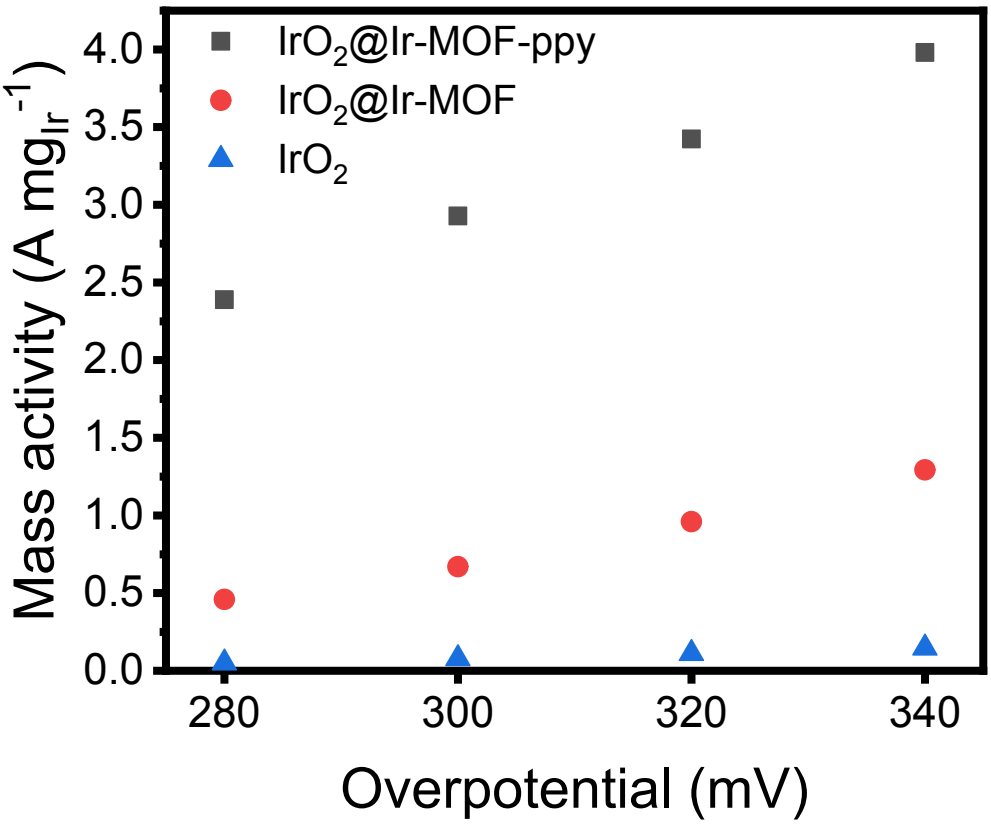


Figure S13. Mass activity of IrO_2@Ir-MOF-ppy, IrO_2@Ir-MOF and IrO_2 at 280, 300, 320, and 340 mV.

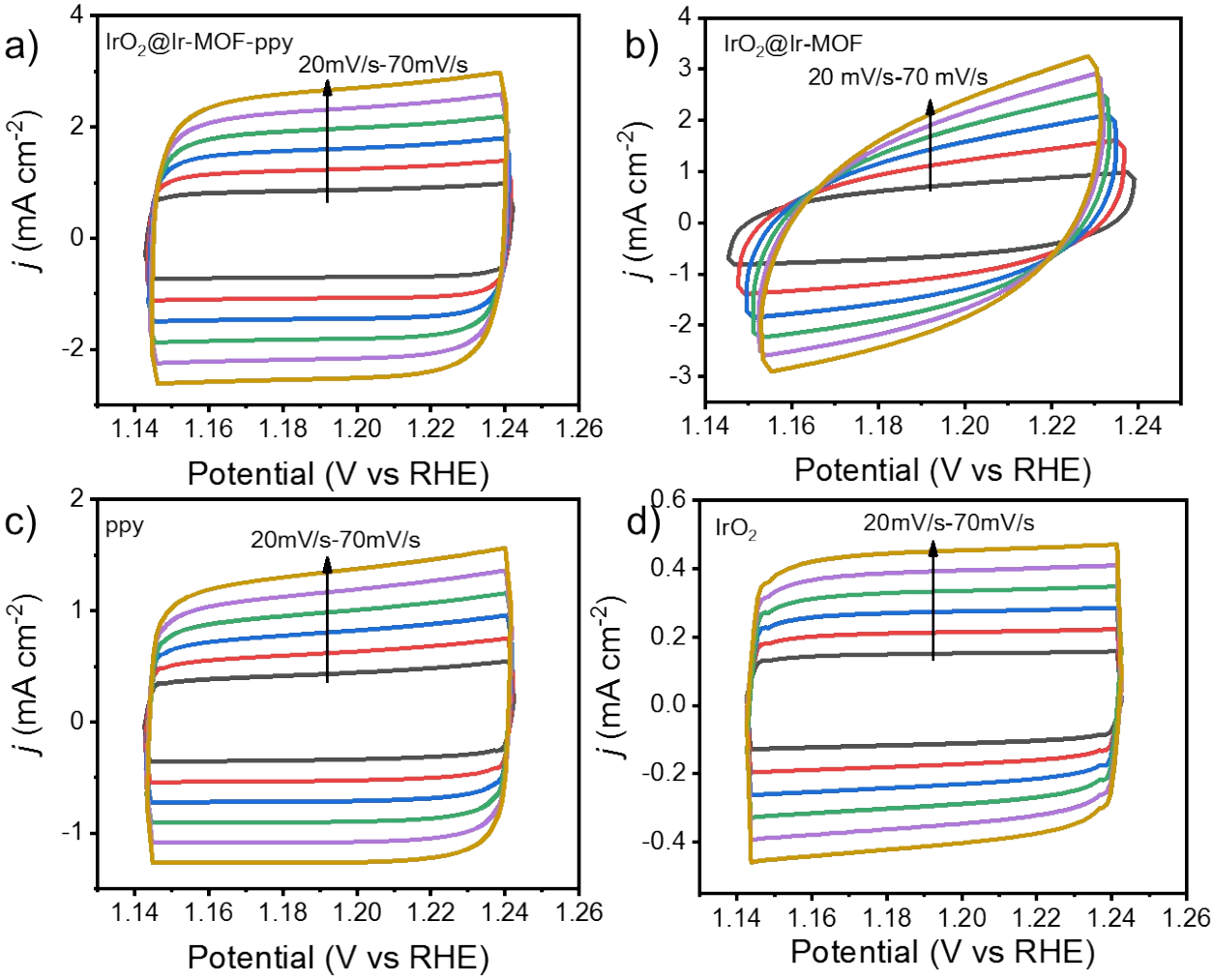


Figure S14. Cyclic voltammograms (CV) of IrO_2@Ir-MOF-ppy, IrO_2@Ir-MOF, ppy and IrO_2 in the window of 1.142~1.242 V *vs*. RHE at various scan rates (20, 30, 40, 50, 60 and 70 mV/s).

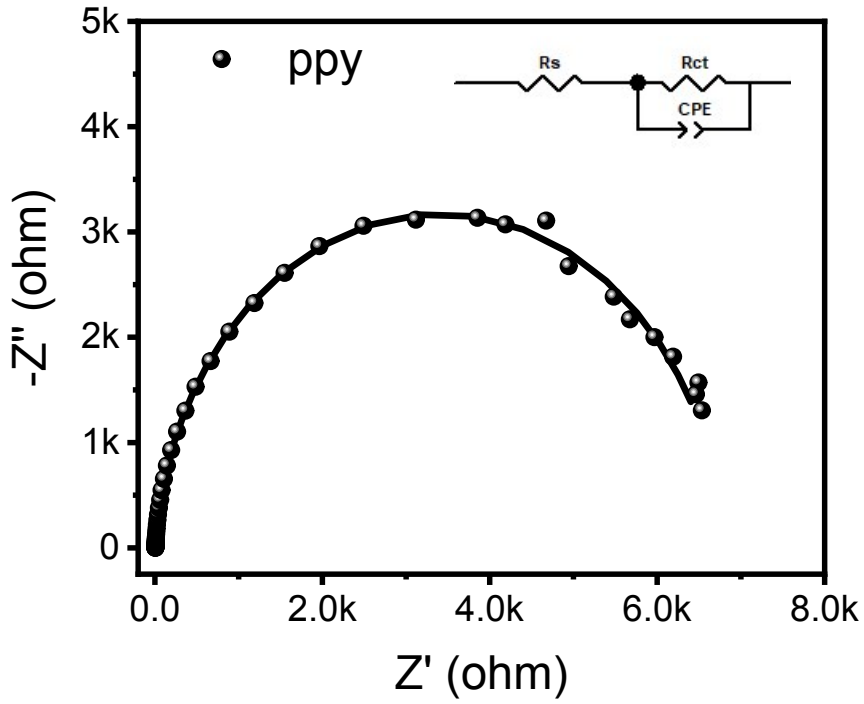


Figure S15. EIS spectra of ppy are recorded at 1.6 V vs. RHE with 5 mV amplitude in a frequency range from 10^5 to 1 Hz

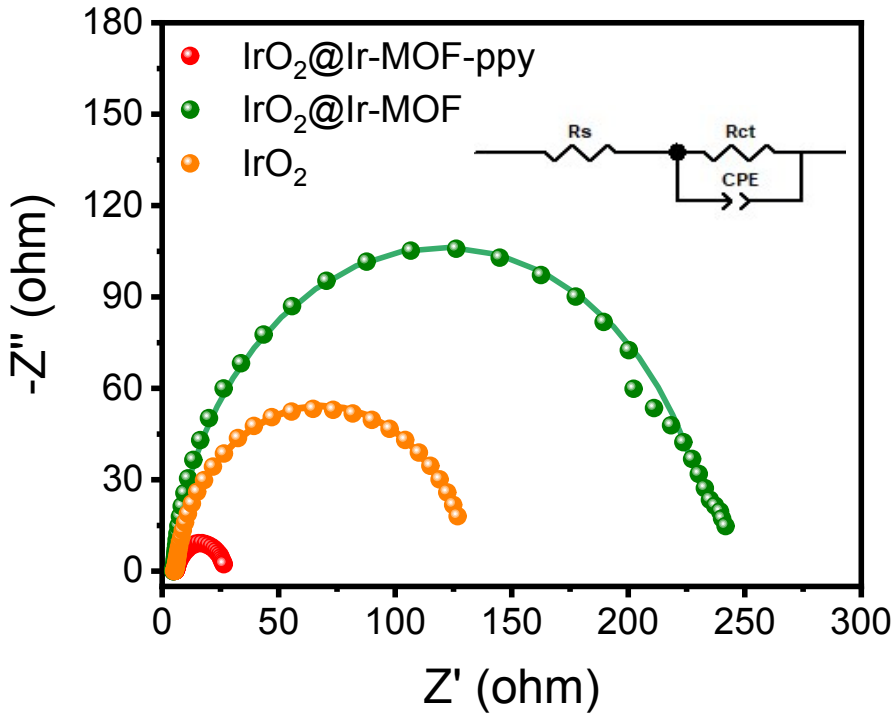


Figure S16. EIS spectra of corresponding catalysts recorded at 1.6 V vs RHE with 5 mV amplitude in a frequency range from 10^5 to 1 Hz.

Table S4. EIS data of various electrodes.

Sample	**R_s/Ω**	**R_{ct}/Ω**
IrO_2@Ir-MOF-ppy	5.553	22.09
IrO_2@Ir-MOF	4.955	230
IrO_2	5.4	126
ppy	4.999	6881

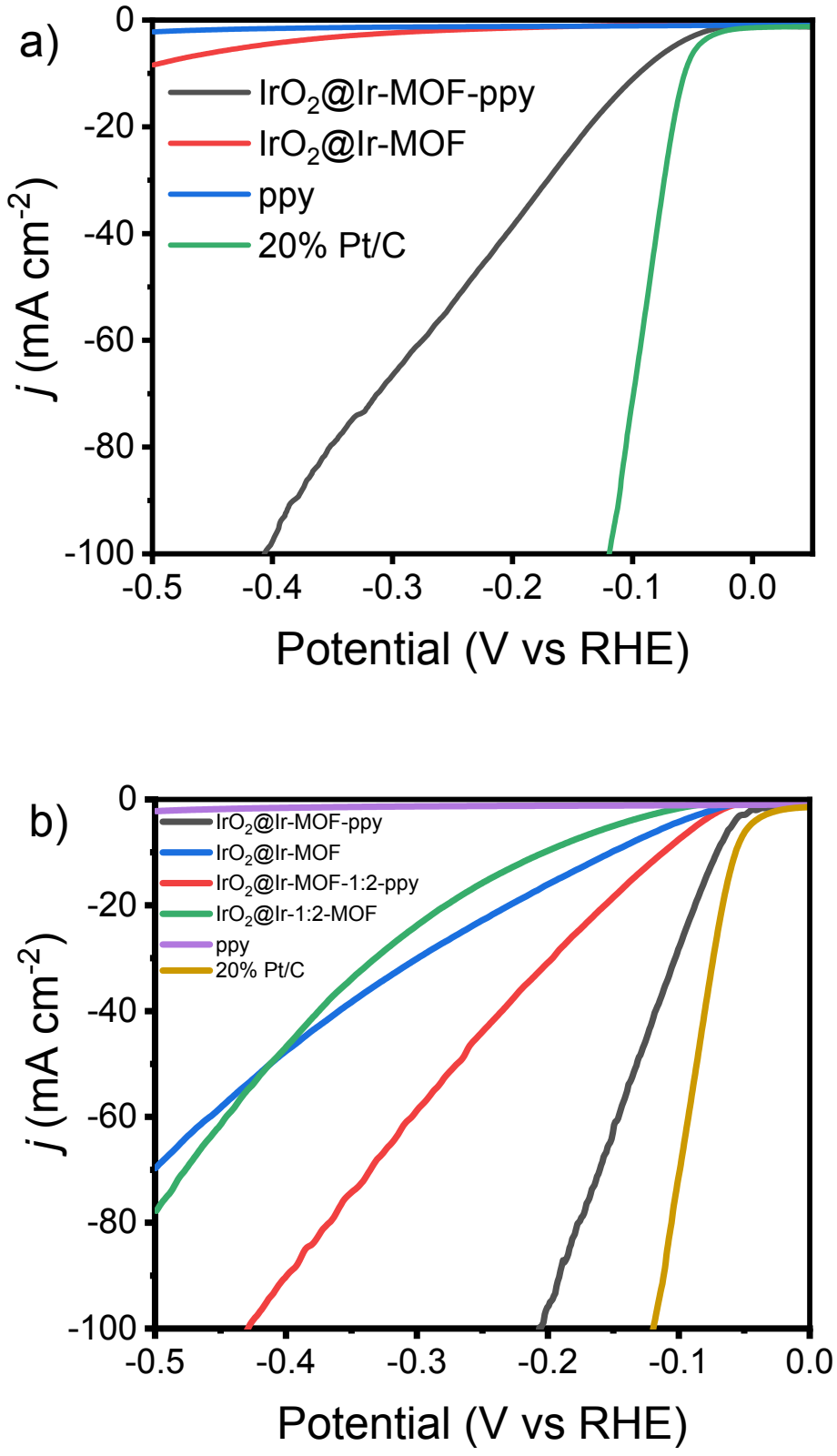


Figure S17. HER polarization curves of IrO_2@Ir-MOF-ppy (a) and IrO_2@Ir-MOF-1:2-ppy (b) with 80% *i*R-compensation in 1 M KOH solution at a scan rate of 5 mV/s.

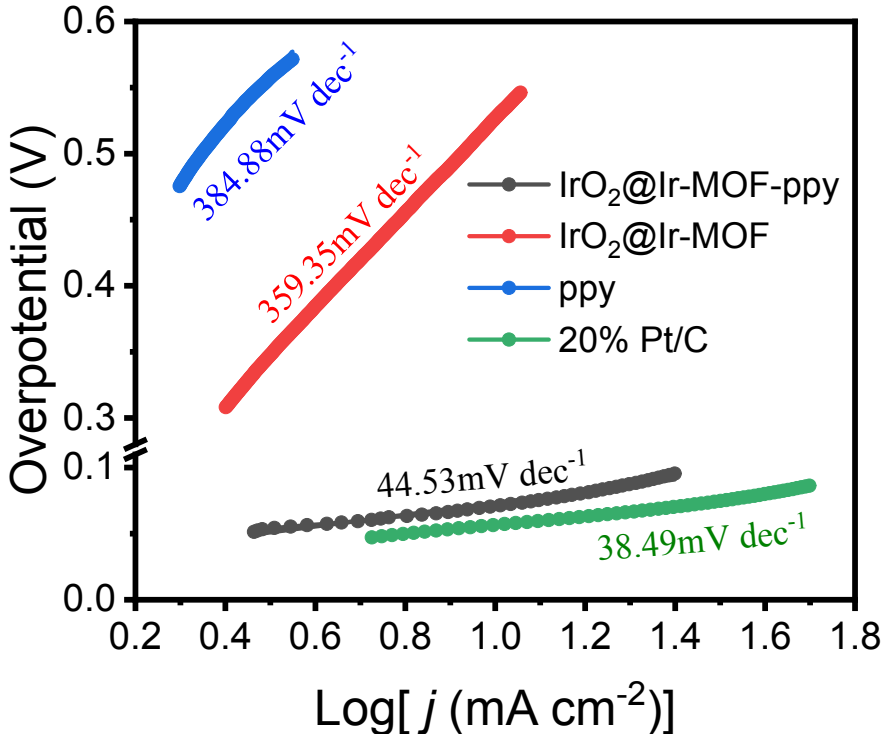


Figure S18. Tafel plots of different catalysts overpotential at different current densities of HER.

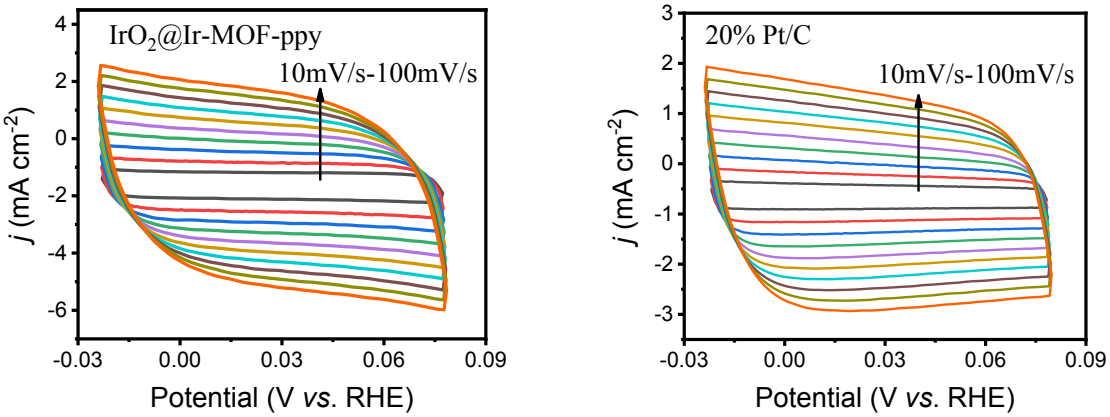


Figure S19. Cyclic voltammograms (CV) curves of IrO_2@Ir-MOF-ppy and 20% Pt/C in the window of -0.022~0.078 V *vs*. RHE at various scan rates (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/s).

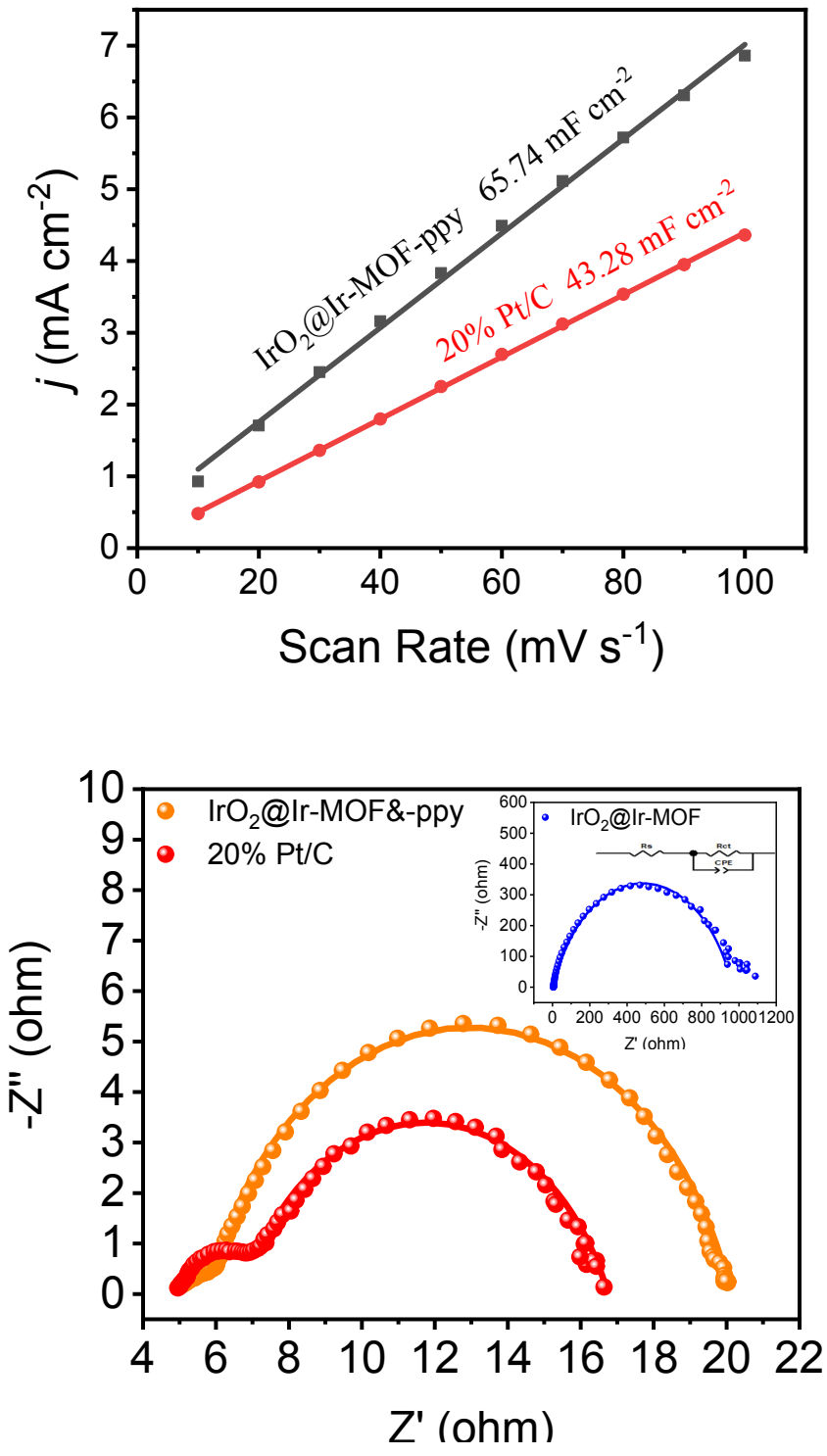


Figure S20. (left) The difference (Δj) between capacitive currents as a function of scan rates to give the double-layer capacitance (C_{dl}) for IrO_2@Ir-MOF-ppy and 20% Pt/C. (right) EIS spectra of corresponding catalysts recorded at an overpotential of 150 mV with 5 mV amplitude in a frequency

range from 10^5 to 1 Hz.

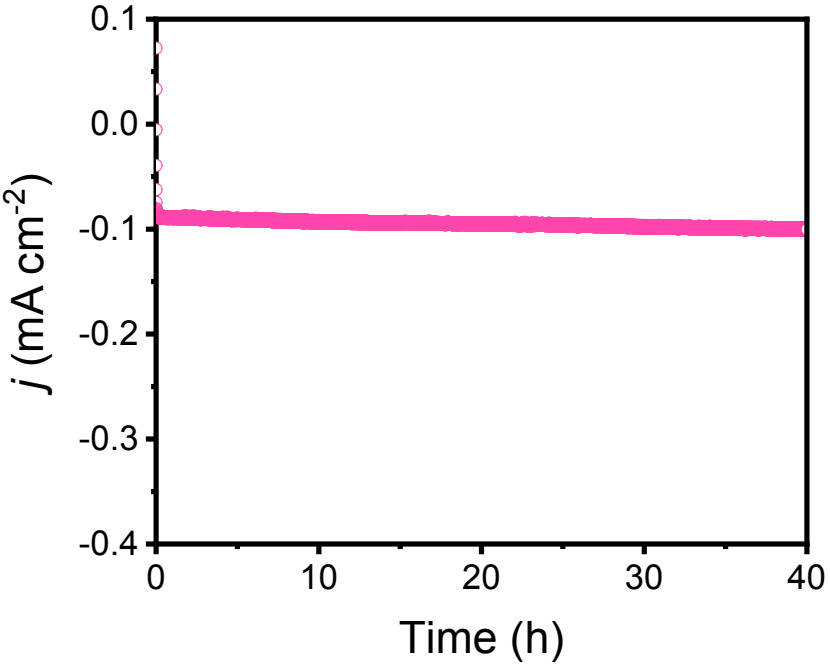


Figure S21. The stability test of IrO_2@Ir-MOF-ppy for HER at the current density around 10 mA/cm^2 in 1M KOH with 80% *i*R-compensation.

Table S5. Summary of the recently reported water splitting electrocatalysts in 1 M KOH electrolytes.

Anode	**Cathode**	**Cell voltage /V**	**Ref**
IrO_2@Ir-MOF	IrO_2@Ir-MOF	1.53	This work
RuO_2	Pt/C	1.55	*Angew. Chem. Int. Ed.* **2017**, 56, 573−577
Pt-CoS_2	Pt-CoS_2	1.55	*Adv. Energy Mater.* **2018**, 8, 1800935
Ir/MoS_2	Ir/MoS_2	1.60	*ACS Energy Lett.* **2019**, *4*, 368-374
Pt-IrO_2/CC	IrO_2/CC	1.492	*Adv. Energy Mater.* **2020**, 2001600
Ru NWs	Ir NWs	1.47	*Adv. Funct. Mater.* **2018**, 28, 1803722
RuCu NSs/C-350 °C	RuCu NSs/C-250 °C	1.49	*Angew. Chem. Int. Ed.* **2019**, 58, 2-8

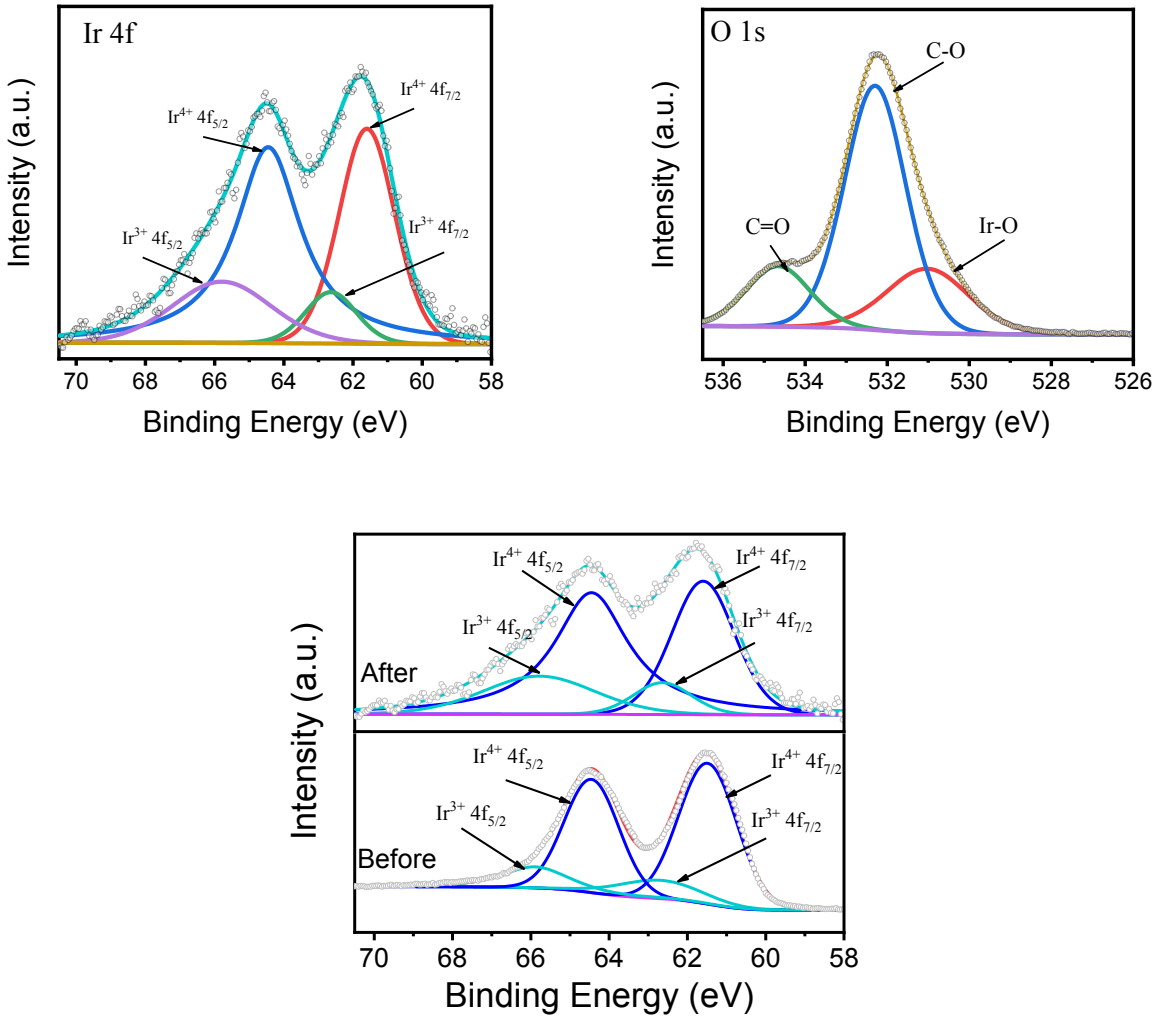


Figure S22. XPS spectra of IrO_2@Ir-MOF after OER.

Table S6. The XPS peak position of IrO_2@Ir-MOF before and after OER.

After OER		**Before OER**	
Ir^{4+} $4f_{7/2}$	61.6	**Ir^{4+} $4f_{7/2}$**	61.5
Ir^{4+} $4f_{5/2}$	64.5	**Ir^{4+} $4f_{5/2}$**	64.5
Ir^{3+} $4f_{7/2}$	62.7	**Ir^{3+} $4f_{7/2}$**	62.6
Ir^{3+} $4f_{5/2}$	65.7	**Ir^{3+} $4f_{5/2}$**	65.9
O-Ir	531	**O-Ir**	530.8
O-C	532.3	**O-C**	532.0
O=C	533.7	**O=C**	533.4

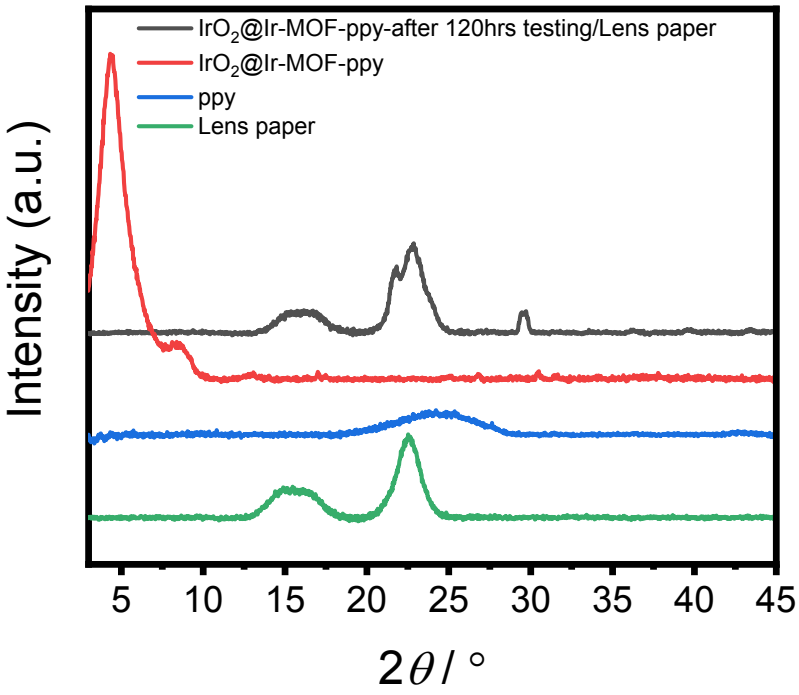


Figure S23. PXRD pattern of IrO_2@Ir-MOF-ppy after long-term water splitting experiment.

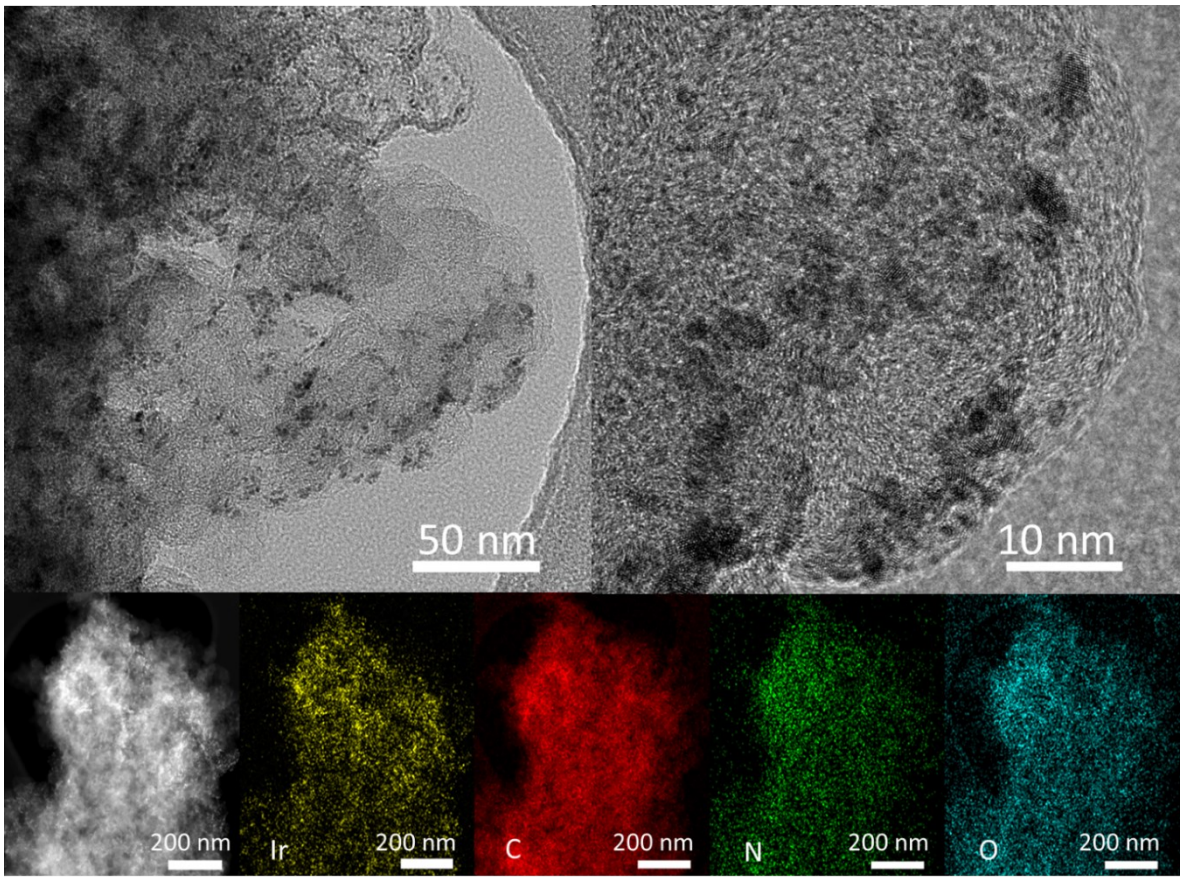


Figure S24. TEM images of IrO_2@Ir-MOF-ppy after long-term water splitting experiment.

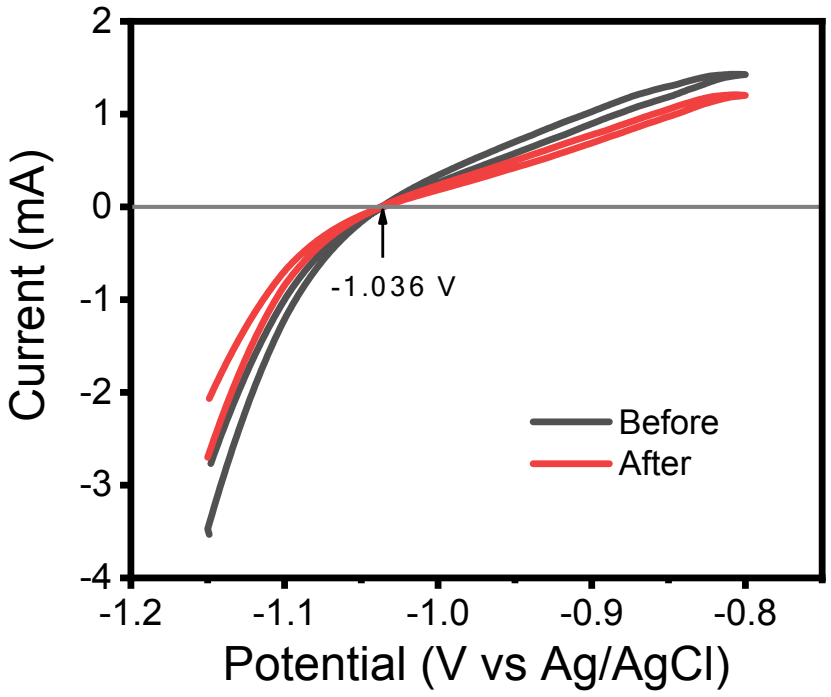


Figure S25. RHE correction diagram of Ag/AgCl reference electrode used in the experiment in 1 M KOH system before and after long-term water splitting experiment.