

Cracked Carbon Matrix Decorated with Amorphous IrO_x Boosting Oxygen Evolution Reaction in Electrochemical Water Splitting

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Supplementary Figures

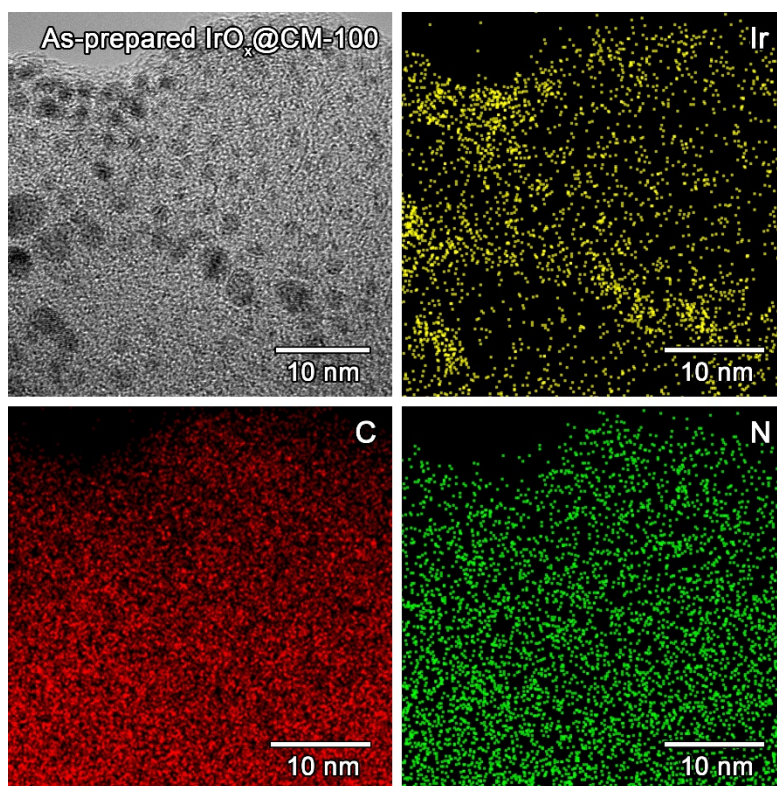


Figure S1. A TEM image and elemental mapping results of Ir nanoparticle embedded in CM-100.

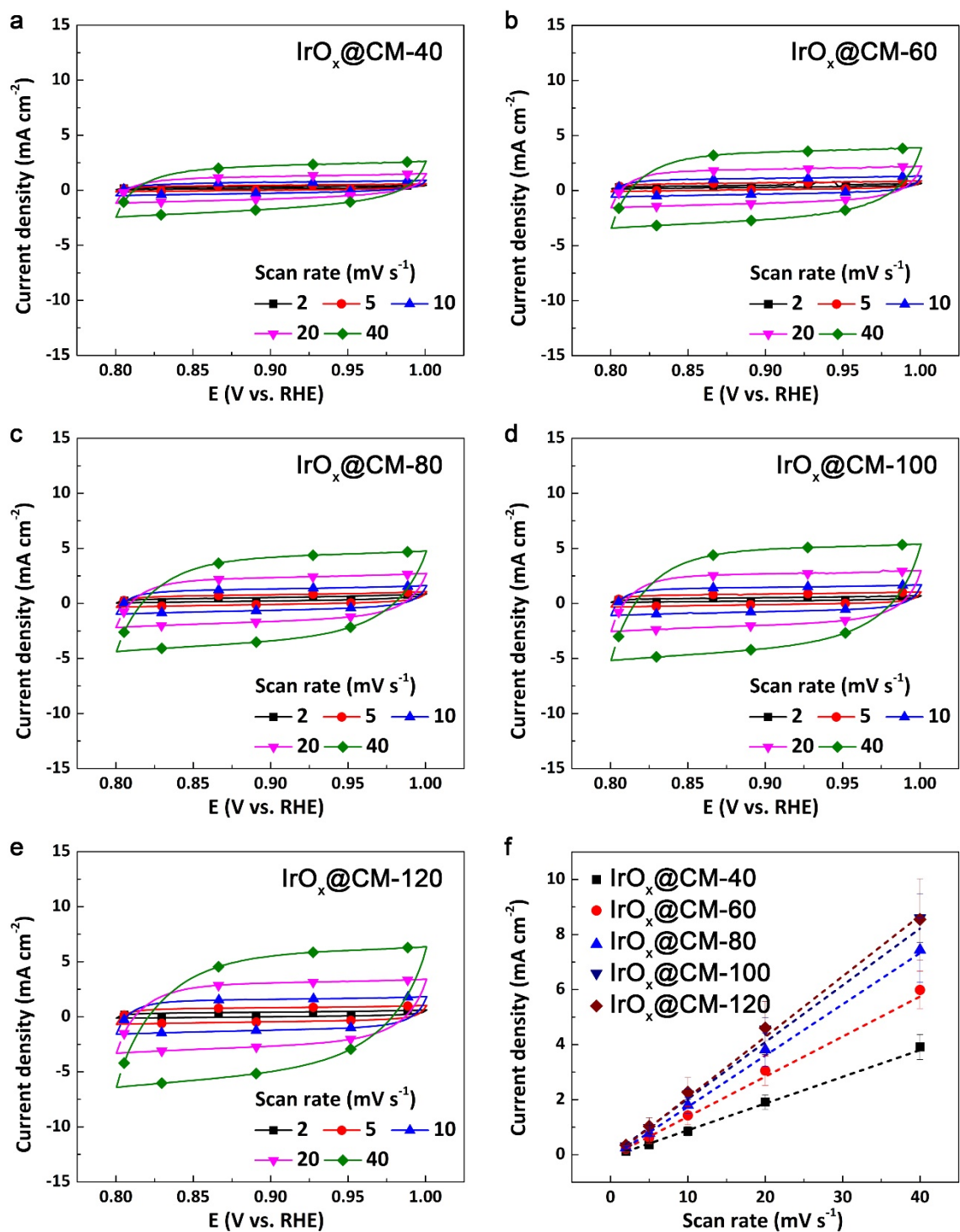


Figure S2. Cyclic voltammograms for (a) IrO_x@CM-40, (b) 60, (c) 80, (d) 100, and (e) 120 for measuring ECSA. (f) Current density as a function of the scan rate measured from (a)–(e).

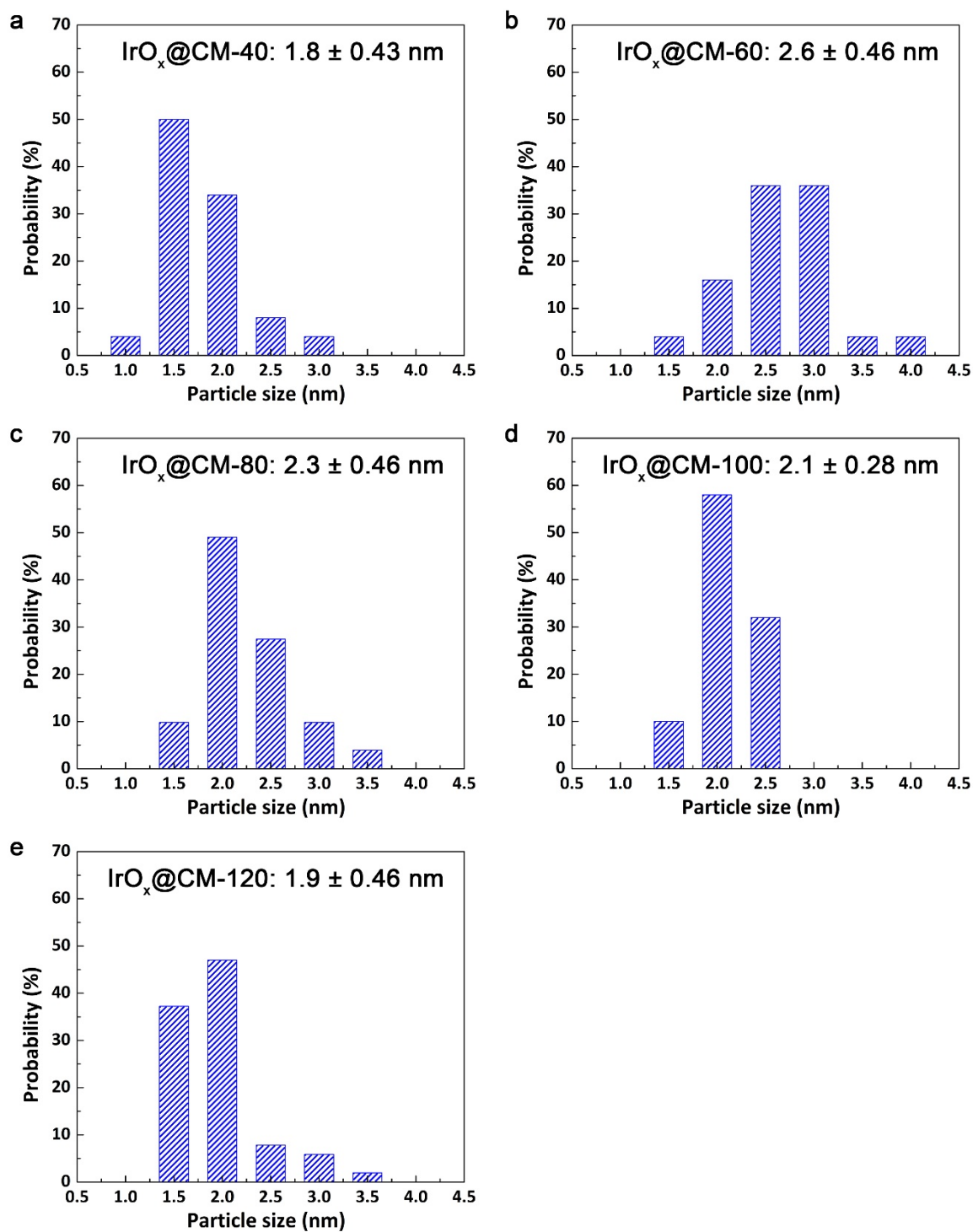


Figure S3. Size distribution of IrO_x nanoparticles embedded in (a) CM-40, (b) 60, (c) 80, (d) 100, and (e) 120.

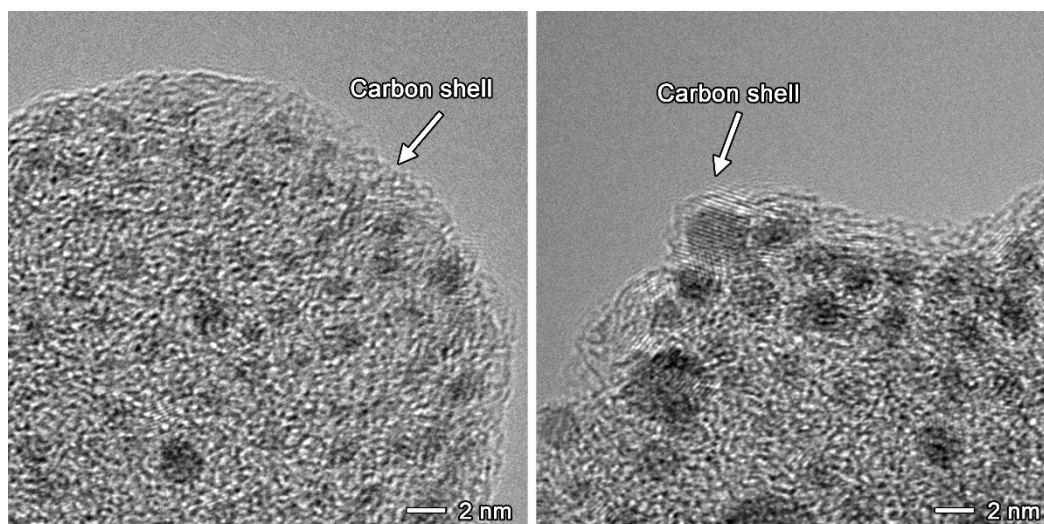


Figure S4. TEM images for IrO_x@CM-100 with white arrows indicating thin carbon layers on IrO_x particles.

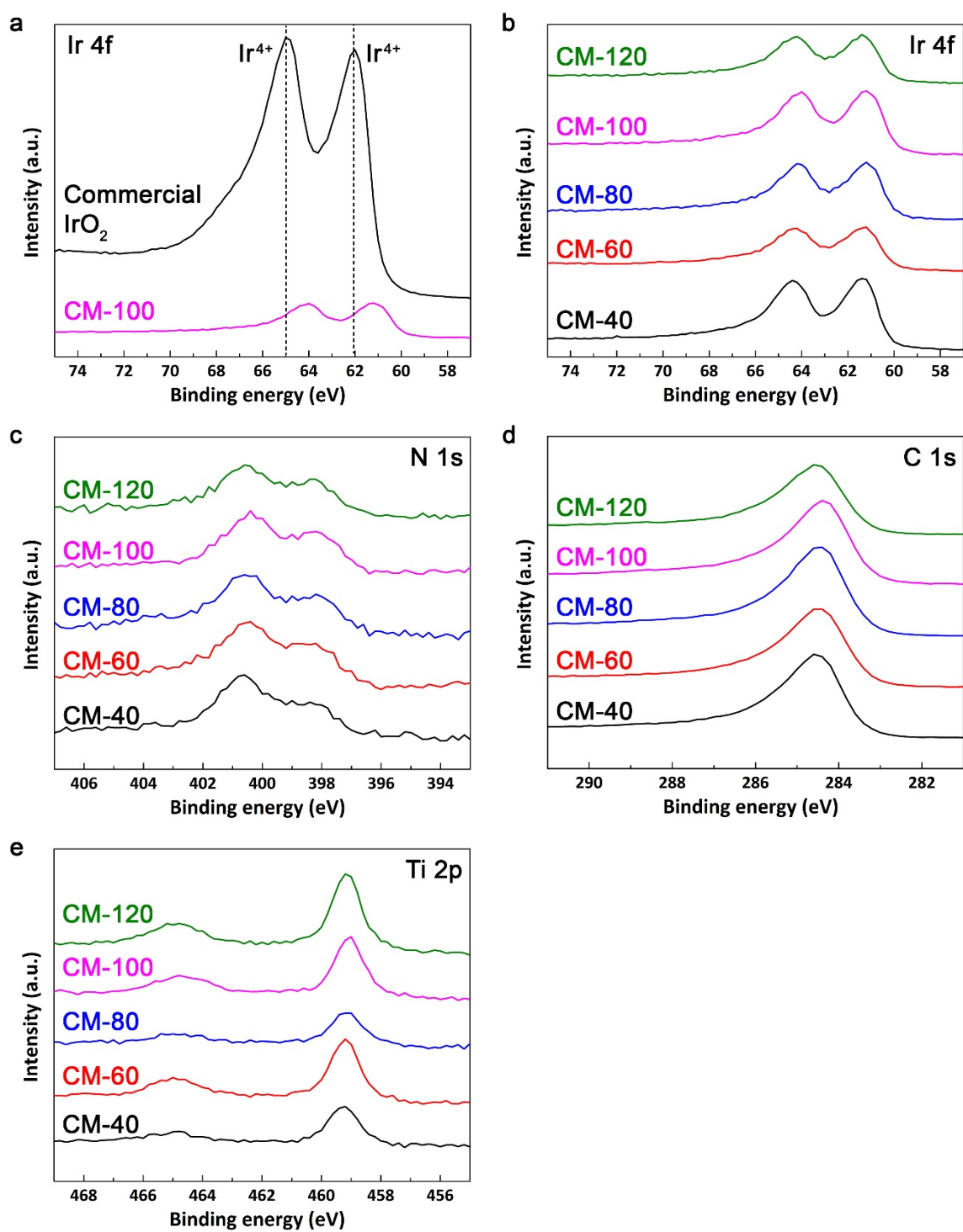


Figure S5. (a) XPS spectra of Ir 4f for commercial IrO_2 and synthesized IrO_x nanoparticles with IrO_x @CM-100. XPS spectra of (b) Ir 4f, (c) N 1s, (d) C 1s, and (e) Ti 2p for IrO_x @CM-40, 60, 80, 100, and 120.

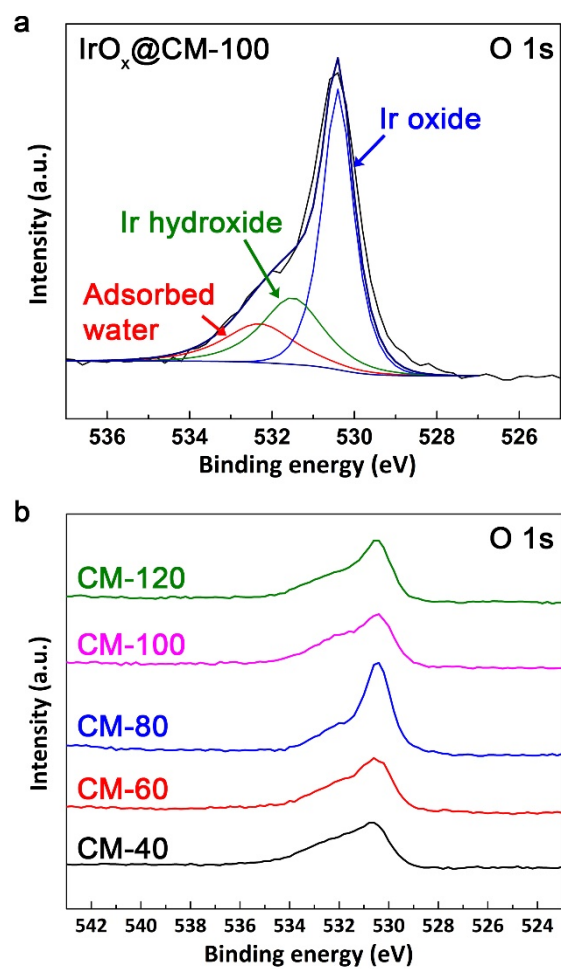


Figure S6. XPS spectra of O 1s for (a) IrO_x@CM-100 and (b) IrO_x@CM samples.

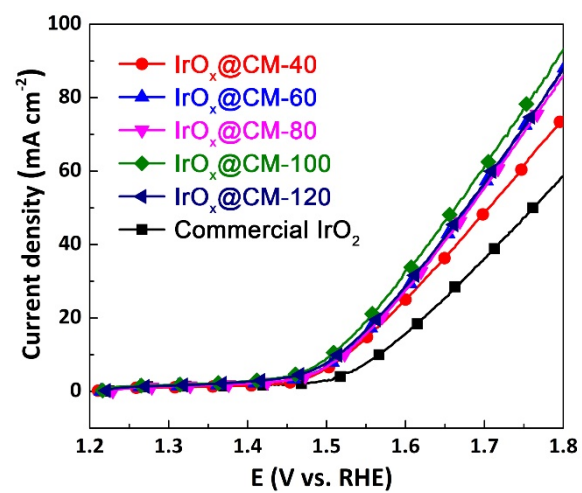


Figure S7. Voltammograms before IR correction for OER on commercial IrO₂ and IrO_x@CM samples.

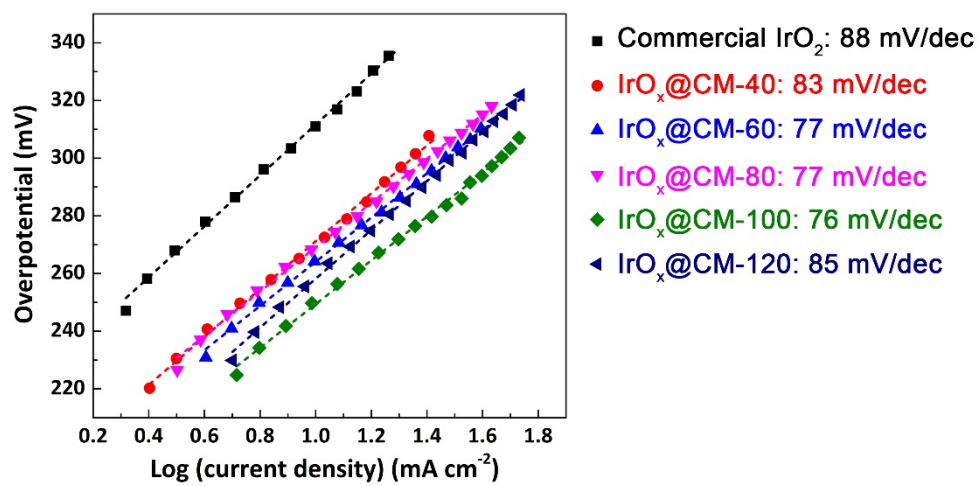


Figure S8. Tafel plots for commercial IrO₂ and IrO_x@CM samples.

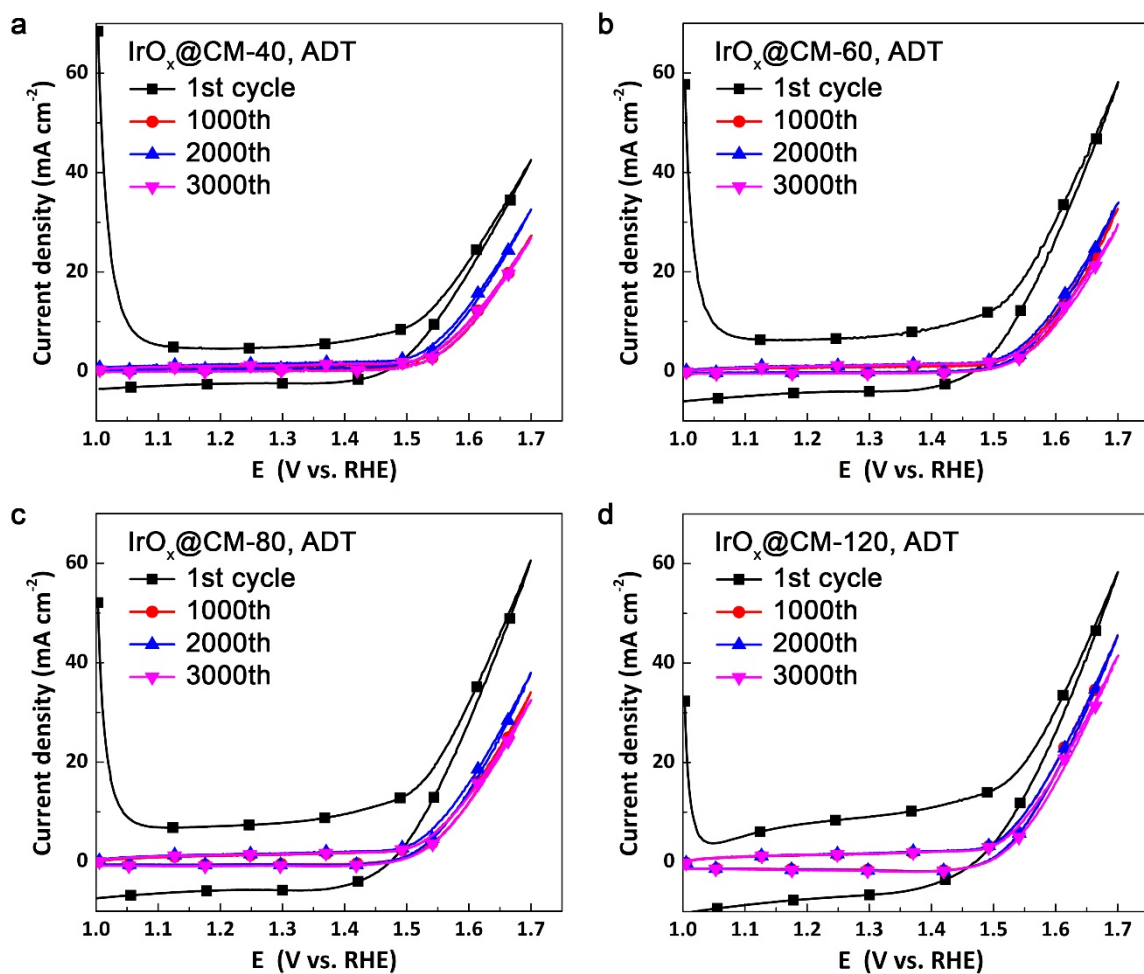


Figure S9. Voltammograms during the accelerated durability test (ADT) for (a) IrO_x@CM-40, (b) 60, (c) 80, and (d) 120 in N₂-saturated 0.1 M HClO₄ electrolyte.

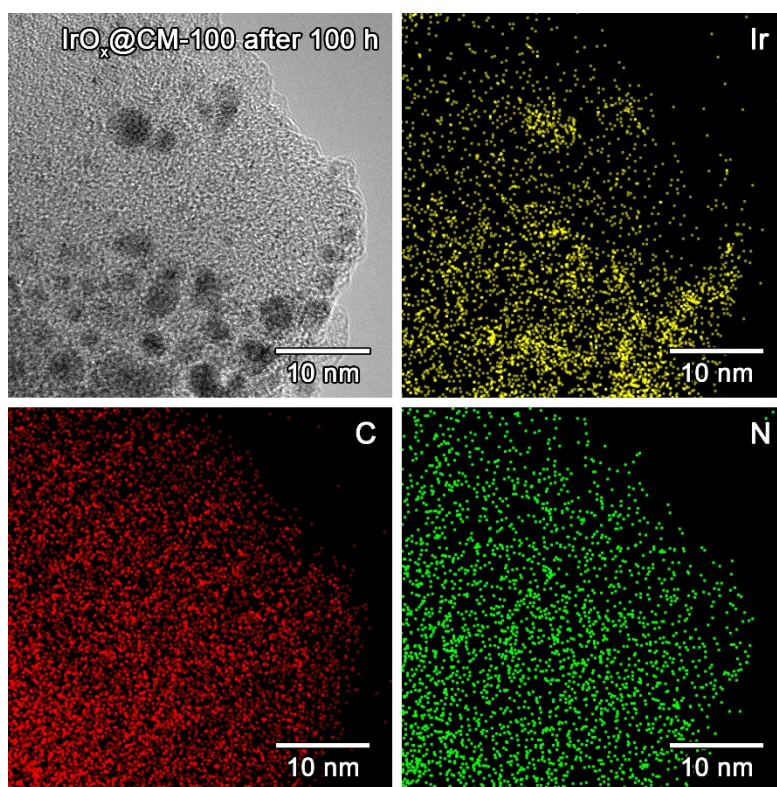


Figure S10. A TEM image and elemental mapping results of IrO_x@CM-100 after long-term durability test at 10 mA·cm⁻² for 100 h.

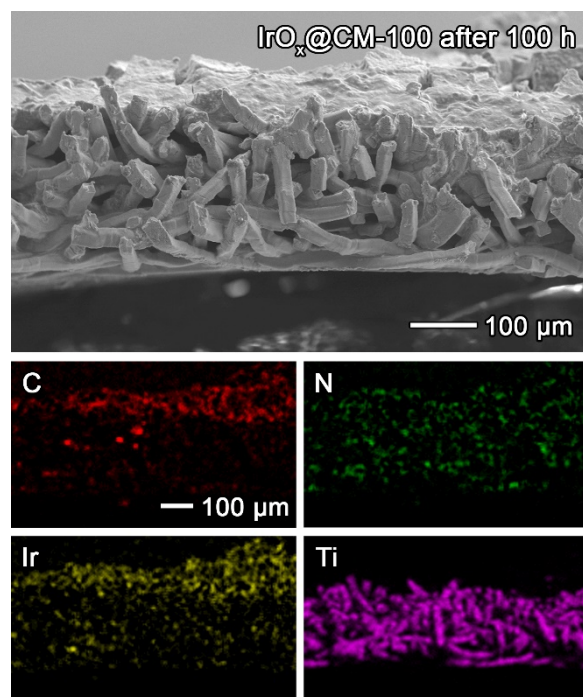


Figure S11. A SEM image and elemental mapping results of $\text{IrO}_x@\text{CM-100}$ after long-term durability test at $10 \text{ mA}\cdot\text{cm}^{-2}$ for 100 h.

Supplementary Tables

Table S1. The Synthetic Conditions for N-Doped Carbon Matrix with IrO_x Nanoparticles.

Samples	The amount of polyaniline solution ^a ($\mu\text{L}\cdot\text{cm}^{-2}$)
IrO _x @CM-40	40
IrO _x @CM-60	60
IrO _x @CM-80	80
IrO _x @CM-100	100
IrO _x @CM-120	120

^aPolyaniline solution: 0.06 M aniline, 0.12 M F-aniline, 1 M HCl, 0.23 M (NH₄)₂S₂O₈
(See Experimental section)

Table S2. OER Half-Cell Performance of Ir-Based Electrocatalysts Reported in Previous Research.

Catalysts	Electrolytes	Loading Amount (mg _{Ir} ·cm ⁻²)	η^a	Stability test		Ref.
				Chronopotentiometry	Increasing rate of η	
IrO_x@CM-100	0.1 M HClO₄	0.5	264	10 mA·cm⁻², 100 h	0.57 mV·h⁻¹	This study
IrO ₂ -Ta ₂ O ₅ /Ti felts	0.1 M H ₂ SO ₄	0.7	270	-	-	1
10% F-doped IrO ₂ /Ti foil	0.1 N H ₂ SO ₄	0.3	250	-	-	2
2% IrO ₂ /NWCNT	0.5 M H ₂ SO ₄	0.016	272	10 mA·cm ⁻² , 12 h	3.6 mV·h ⁻¹	3
4wt % IrO ₂ /CNT	0.1 M H ₂ SO ₄	0.076	270	10 mA·cm ⁻² , 12 h	3.8 mV·h ⁻¹	4
IrW/C	0.1 M HClO ₄	0.03	300 ^b	-	-	5
Ir superstructure/VC	0.1 M HClO ₄	0.0115	276	10 mA·cm ⁻² , 5 h	7.8 mV·h ⁻¹	6
IrNiCu /CB	0.1 M HClO ₄	0.02	303	-	-	7
IrO ₂ nanofiber	0.1 M H ₂ SO ₄	0.2	440	-	-	8
IrO ₂ -RuO ₂ @Ru	0.5 M H ₂ SO ₄	0.379	281	-	-	9
IrO _x nanosheets	0.5 M H ₂ SO ₄	0.0078	250	10 mA·cm ⁻² , 10 h	4.7 mV·h ⁻¹	10
3-DOM IrO ₂	0.5 M H ₂ SO ₄	0.127	330	-	-	11
IrO ₂ /CNT	0.5 M H ₂ SO ₄	0.016	293	10 mA·cm ⁻² , 10 h	5.7 mV·h ⁻¹	12
Ir nanoparticles/graphene	0.5 M H ₂ SO ₄	0.82	290	10 mA·cm ⁻² , 10 h	5.0 mV·h ⁻¹	13
Mesoporous IrO ₂ film	0.1 M HClO ₄	-	270	-	-	14
IrO ₂ /graphitic carbon nitride	0.5 M H ₂ SO ₄	0.081	276	20 mA·cm ⁻² , 4 h	3.4 mV·h ⁻¹	15
Ir ₇₀ Ni ₁₅ Co ₁₅	0.1 M HClO ₄	0.25	220	10 mA·cm ⁻² , 24 h	1.4 mV·h ⁻¹	16

^aOverpotential@10 mA·cm⁻² (mV)

Table S3. Charge Transfer and Solution Resistances Measured from Nyquist Plots in Figure 4(c).

Samples	Solution resistance (R_s, $\Omega \cdot \text{cm}^2$)	Film resistance (R_f, $\Omega \cdot \text{cm}^2$)	Charge transfer resistance (R_{ct}, $\Omega \cdot \text{cm}^2$)
IrO _x @CM-40	2.90	1.38	5.35
IrO _x @CM-60	2.60	1.30	3.24
IrO _x @CM-80	2.64	1.03	3.76
IrO _x @CM-100	2.60	0.17	3.20
IrO _x @CM-120	2.56	0.84	3.90
Commercial IrO ₂	2.53	2.02	10.82

Table S4. Percentages of Oxygen Species Calculated from XPS Spectra in Figure S6(b).

Samples	Lattice O	OH group
IrO _x @CM-40	49.5	50.5
IrO _x @CM-60	54.1	45.9
IrO _x @CM-80	52.5	47.5
IrO _x @CM-100	46.2	53.8
IrO _x @CM-120	54.0	46.0

Table S5. Full-Cell Performance of Ir-Based Electrocatalysts Reported in Previous Research.

Catalysts		Membrane	T _{cell} (°C)	Cell voltage @1A·cm ⁻² (V)	Ref.
Anode	Cathode				
IrO_x@CM-100 (1 mg·cm⁻²)	Pt/C 40% (0.4 mg·cm⁻²)	NR115	90	1.64	This study
Ir/TiO ₂ -MoO _x (0.5 mg·cm ⁻²)	Pt/C 46% (0.5 mg·cm ⁻²)	NR212	80	1.74	17
Ir/B4C-100 °C (0.5 mg·cm ⁻²)	Pt/C 20% (0.4 mg·cm ⁻²)	NR212	80	1.63	18
Ir _{0.7} Ru _{0.3} O _x (1.8 mg·cm ⁻²)	Pt/C (0.5 mg·cm ⁻²)	NR115	80	1.656	19
IrO ₂ (1.4 mg·cm ⁻²)	Pt/C 40% (0.4 mg·cm ⁻²)	NR115	80	1.765	20
IrO ₂ (3.0 mg·cm ⁻²)	Pt/C (0.1 mg·cm ⁻²)	NR212	RT	1.56	21
Ir _{0.52} Sn _{0.48} O ₂ (1.5 mg·cm ⁻²)	Pt/C 70% (0.57 mg·cm ⁻²)	NR115	80	1.63	22
IrO ₂ @TiO ₂ (1.2 mg·cm ⁻²)	Pt/C 60% (0.5 mg·cm ⁻²)	NR115	80	1.7	23
IrO ₂ -V doped TiO ₂ (2.5 mg·cm ⁻²)	Pt/C 40% (0.5 mg·cm ⁻²)	NR117	80	2.03	24
IrO ₂ -Nb doped TiO ₂ (2.5 mg·cm ⁻²)	Pt/C 40% (0.5 mg·cm ⁻²)	NR117	80	2.027	25
IrO ₂ (1.7 mg·cm ⁻²)	Pt/C 40% (0.5 mg·cm ⁻²)	NR117	80	1.88	26
80% IrO ₂ /ATO (2 mg·cm ⁻²)	Pt/C 20% (0.5 mg·cm ⁻²)	NR115	80	1.74	27

References

- 1 F. Amano, Y. Furusho and Y. M. Hwang, *ACS Appl. Energy Mater.*, 2020, **3**, 4531–4538.
- 2 K. S. Kadakia, P. H. Jampani, O. I. Velikokhatnyi, M. K. Datta, S. K. Park, D. H. Hong, S. J. Chung and P. N. Kumta, *J. Power Sources*, 2014, **269**, 855–865.
- 3 X. Wen, L. Bai, M. Li and J. Guan, *Mater. Today Energy*, 2018, **10**, 153–160.
- 4 R. Badam, M. Hara, H. H. Huang and M. Yoshimura, *Int. J. Hydrogen Energy*, 2018, **43**, 18095–18104.
- 5 F. Lv, J. Feng, K. Wang, Z. Dou, W. Zhang, J. Zhou, C. Yang, M. Luo, Y. Yang, Y. Li, P. Gao and S. Guo, *ACS Cent. Sci.*, 2018, **4**, 1244–1252.
- 6 Y. Pi, N. Zhang, S. Guo, J. Guo and X. Huang, *Nano Lett.*, 2016, **16**, 4424–4430.
- 7 J. Park, Y. J. Sa, H. Baik, T. Kwon, S. H. Joo and K. Lee, *ACS Nano*, 2017, **11**, 5500–5509.
- 8 F. Hegge, F. Lombeck, E. Cruz Ortiz, L. Bohn, M. Von Holst, M. Kroschel, J. Hübner, M. Breitwieser, P. Strasser and S. Vierrath, *ACS Appl. Energy Mater.*, 2020, **3**, 8276–8284.
- 9 G. Li, S. Li, J. Ge, C. Liu and W. Xing, *J. Mater. Chem. A*, 2017, **5**, 17221–17229.
- 10 B. Jiang, J. Kim, Y. Guo, K. C. W. Wu, S. M. Alshehri, T. Ahamad, N. Alhokbany, J. Henzie and Y. Yamachi, *Catal. Sci. Technol.*, 2019, **9**, 3697–3702.
- 11 W. Hu, Y. Wang, X. Hu, Y. Zhou and S. Chen, *J. Mater. Chem. View*, 2012, **22**, 6010.
- 12 J. Guan, D. Li, R. Si, S. Miao, F. Zhang and C. Li, *ACS Catal.*, 2017, **7**, 5983–5986.
- 13 J. Zhang, G. Wang, Z. Liao, P. Zhang, F. Wang, X. Zhuang, E. Zschech and X. Feng, *Nano Energy*, 2017, **40**, 27–33.
- 14 E. Ortel, T. Reier, P. Strasser and R. Kraehnert, *Chem. Mater.*, 2011, **23**, 3201–3209.
- 15 J. Chen, P. Cui, G. Zhao, K. Rui, M. Lao, Y. Chen, X. Zheng, Y. Jiang, H. Pan, S. X. Dou and W. Sun, *Angew. Chemie - Int. Ed.*, 2019, **58**, 12540–12544.
- 16 Y. Zhao, M. Luo, S. Chu, M. Peng, B. Liu, Q. Wu, P. Liu, F. M. F. de Groot and Y. Tan, *Nano Energy*, 2019, **59**, 146–153.
- 17 E. J. Kim, J. Shin, J. Bak, S. J. Lee, K. hyun Kim, D. H. Song, J. H. Roh, Y. Lee, H. W. Kim, K. S. Lee and E. A. Cho, *Appl. Catal. B Environ.*, 2021, **280**, 119433.
- 18 J. Islam, S. K. Kim, P. T. Thien, M. J. Kim, H. S. Cho, W. C. Cho, C. H. Kim, C. Lee and J. H. Lee, *J. Power Sources*, 2021, **512**, 230506.
- 19 M. Faustini, M. Giraud, D. Jones, J. Rozière, M. Dupont, T. R. Porter, S. Nowak, M. Bahri, O. Ersen, C. Sanchez, C. Boissière, C. Tard and J. Peron, *Adv. Energy Mater.*, 2019, **9**, 1–11.
- 20 S. Choi, S. H. Shin, D. H. Lee, G. Doo, D. W. Lee, J. Hyun, J. Y. Lee and H. T. Kim, *J. Mater. Chem. A*, 2022, **10**, 789–798.

- 21 H. Su, B. J. Bladergroen, V. Linkov, S. Pasupathi and S. Ji, *Int. J. Hydrogen Energy*, 2011, **36**, 15081–15088.
- 22 G. Li, H. Yu, X. Wang, S. Sun, Y. Li, Z. Shao and B. Yi, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2858–2866.
- 23 C. Van Pham, M. Bühler, J. Knöppel, M. Bierling, D. Seeberger, D. Escalera-López, K. J. J. Mayrhofer, S. Cherevko and S. Thiele, *Appl. Catal. B Environ.*, 2020, **269**, 118762.
- 24 C. Hao, H. Lv, Q. Zhao, B. Li, C. Zhang, C. Mi, Y. Song and J. Ma, *Int. J. Hydrogen Energy*, 2017, **42**, 9384–9395.
- 25 C. Hao, H. Lv, C. Mi, Y. Song and J. Ma, , DOI:10.1021/acssuschemeng.5b00531.
- 26 H. J. Ban, M. Y. Kim, D. Kim, J. Lim, T. W. Kim, C. Jeong, Y. A. Kim and H. S. Kim, *J. Electrochem. Sci. Technol.*, 2019, **10**, 22–28.
- 27 V. K. Puthiyapura, M. Mamlouk, S. Pasupathi, B. G. Pollet and K. Scott, *J. Power Sources*, 2014, **269**, 451–460.