

## Supporting information for

# Structural Modulation of TiO<sub>2</sub> Supports by Cr Doping to Tune Ir Electronic Structure and Accelerate Acidic OER

Chen Cao<sup>a,b,c</sup>, Shirui Cui<sup>a</sup>, Yanqin Li<sup>a</sup>, Chunyang Zhao<sup>a</sup>, Wei Hu<sup>a</sup>, Feng Shi<sup>b,c</sup>, Zelong Li<sup>a\*</sup>, Yu Tang<sup>a\*</sup>

<sup>a</sup>Key Laboratory of Advanced Catalysis, Gansu Province, State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, China

<sup>b</sup>State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences No.18, Tianshui Middle Road, Lanzhou, 730000, China

<sup>c</sup>University of Chinese Academy of Sciences, Beijing 100049, China

Correspondence: Zelong Li (lizl@lzu.edu.cn); Yu Tang (tangyu@lzu.edu.cn)

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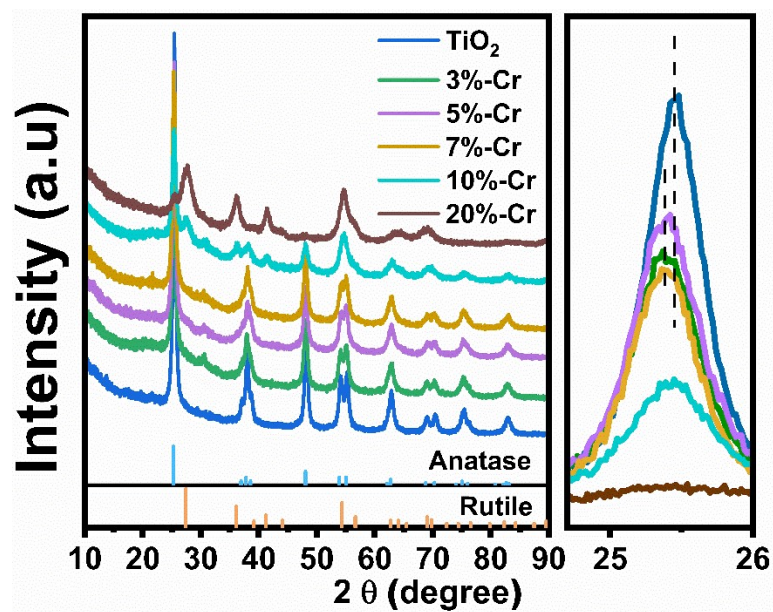


Fig. S1. XRD of catalysts with different contents of Cr.

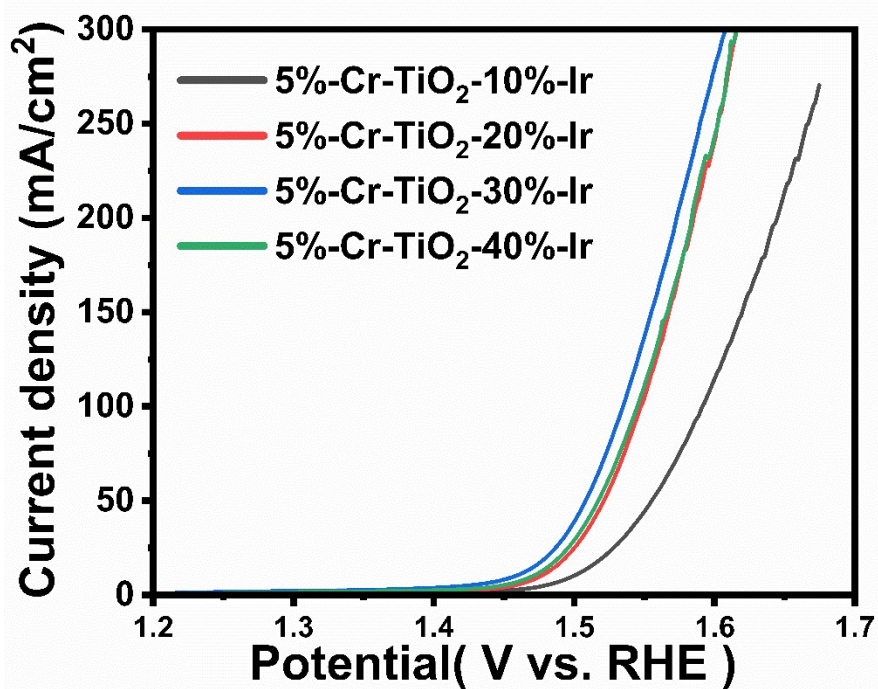


Fig. S2. LSV curves of catalysts with different contents of Ir.

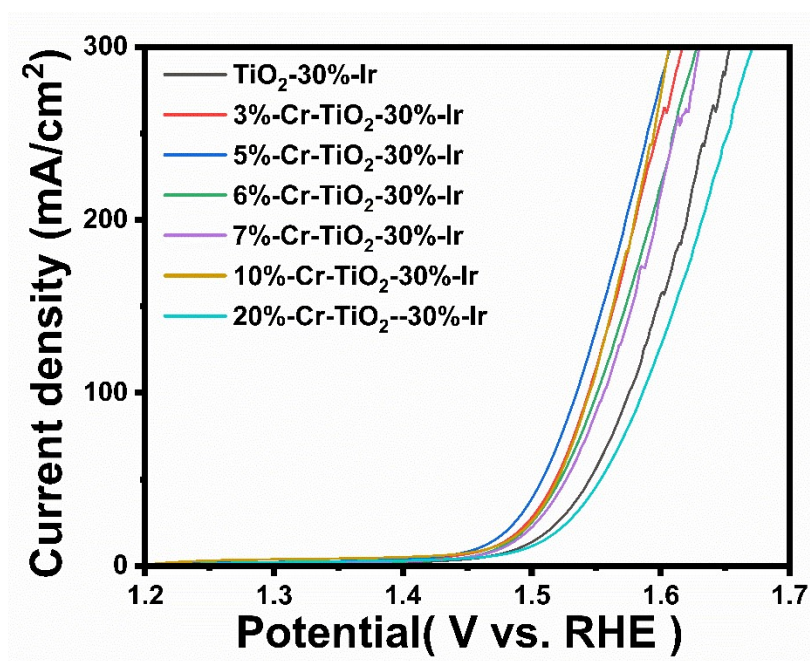


Fig. S3. LSV curves of catalysts with different contents of Cr.

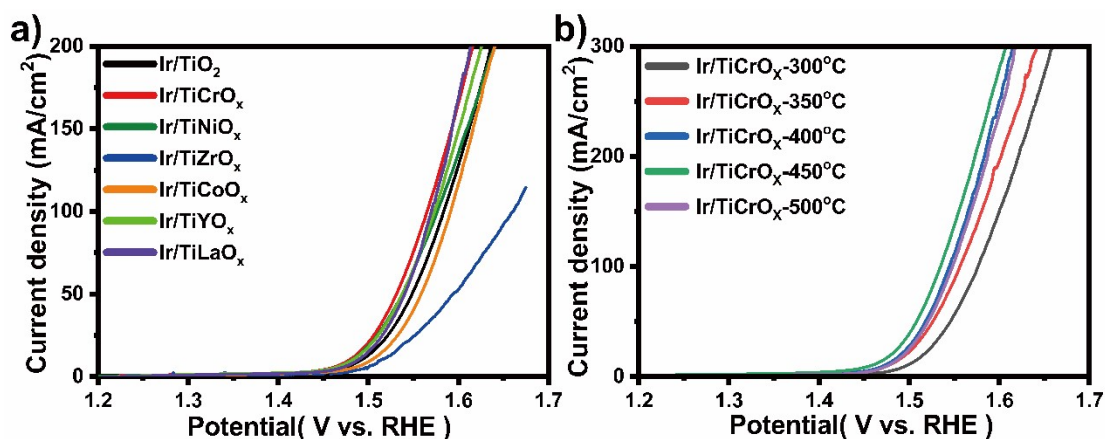


Fig. S4. (a) LSV profiles of catalysts with different elemental doping. (b) LSV profiles of catalysts treated at different heating temperatures.

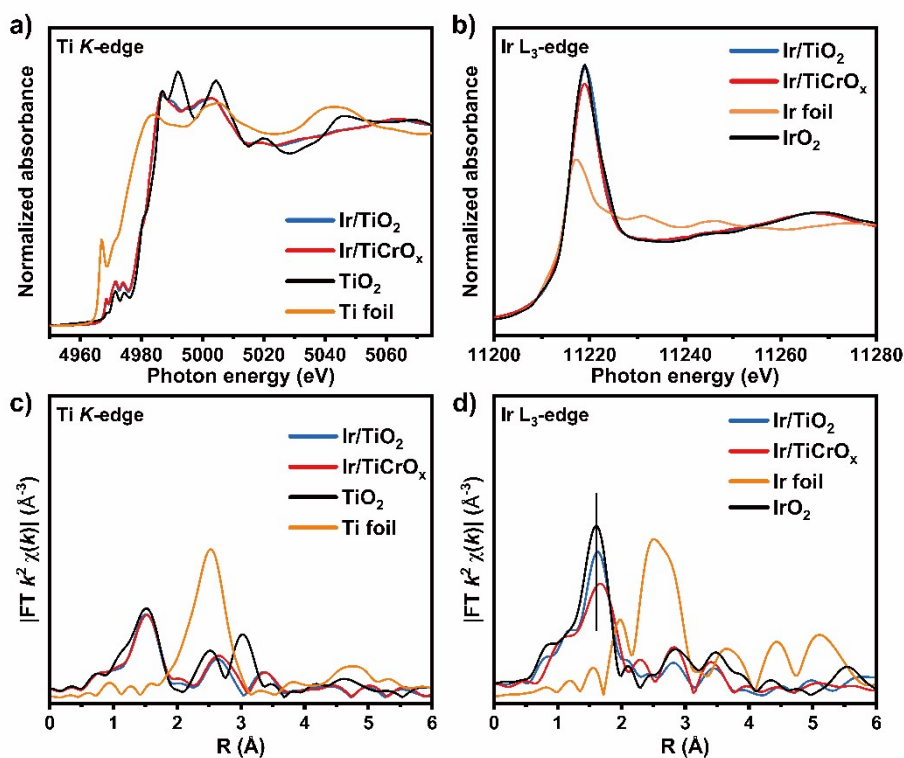


Fig. S5. (a) Ti K-edge and b) Ir  $L_{3}$ -edge XANES spectra of different catalysts. (c) Ti K-edge and (d) Ir  $L_{3}$ -edge FT-EXAFS spectra of different catalysts.

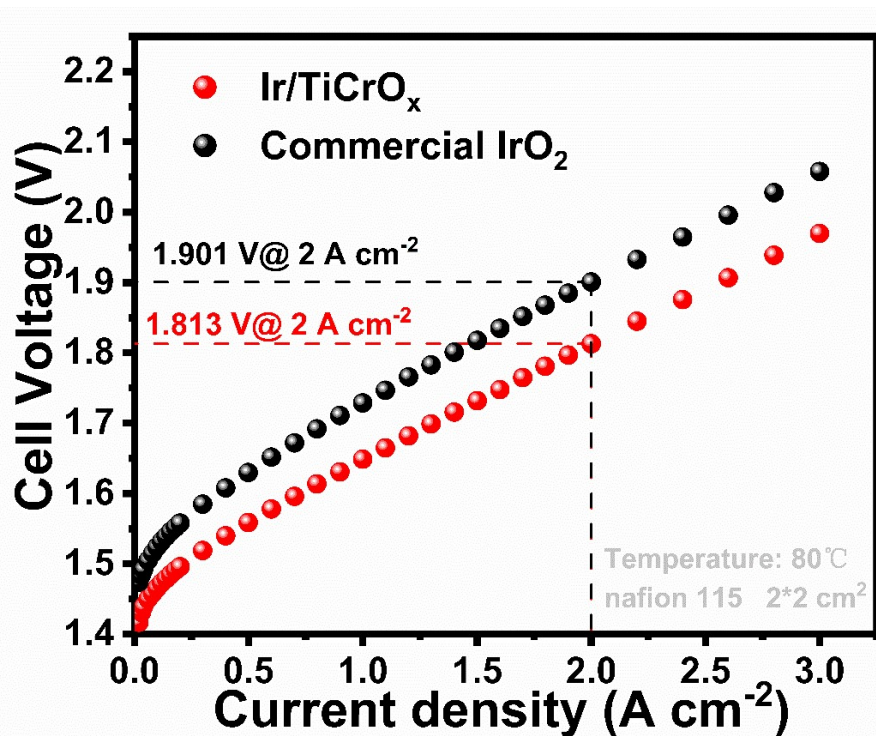


Fig. S6. Steady-state polarization curves of PEMWE using Ir/TiCrO<sub>x</sub> and commercial IrO<sub>2</sub> as anode catalysts.

Table S1. Parameters used in EXAFS fittings.

Sample	Shell	Bond length (Å)	Coordination Number	$\sigma^2$ (Å <sup>2</sup> )	E <sub>0</sub> shift (eV)	R-factor
Ir/TiO <sub>2</sub>	Ti-O	1.94±0.02	5.8±0.6	0.002±0.001	-	0.020
	Ti-Ti	3.04±0.02	4.0±0.7	0.004±0.002	1.6±2.7	
	Ir-O	2.01±0.01	5.7±0.7	0.005±0.002	2.9±1.2	0.018
	Ir-Ir	3.12±0.04	1.8±0.3	0.009±0.006		
Ir/TiCrO <sub>x</sub>	Ti-O	1.96±0.01	5.7±0.5	0.004±0.001	4.5±1.6	0.006
	Ti-Ti	3.05±0.03	4.2±0.5	0.009±0.003		
	Ir-O	2.02±0.03	5.3±0.4	0.009±0.005	2.3±2.2	0.019
	Ir-Ir	3.13±0.01	2.1±0.2	0.013±0.002		

[a]. The value of the amplitude reduction factor ( $S_0^2$ ) was fixed to 0.80; [b]. Bond length is the interatomic distance; [c]. CN is the coordination number; [d].  $\sigma^2$  is Debye-Waller factor (a measure of thermal and static disorder in absorber scatter distance); [e]. E<sub>0</sub> shift is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model); [f]. R factor is used to value the goodness of the fitting; \* This value was fixed during EXAFS fitting, based on the known structure of Ti and Ir.

Table S2. Comparison of various PEMWE operation conditions and catalyst performances.

Catalyst	Anode loading (mg cm <sup>-2</sup> )	Cell activity (V @ A cm <sup>-2</sup> )	Total time	Refs.
Ir/TiCrO <sub>x</sub>	0.5	1.73 V @ 2 A cm <sup>-2</sup> 1.60 V @ 1 A cm <sup>-2</sup>	350 h @ 2 A cm <sup>-2</sup>	This work
RIE-Ir/CeO <sub>x</sub>	0.4	1.62 V @ 2 A cm <sup>-2</sup>	2000 h @ 1 A cm <sup>-2</sup>	[1]
IrVI -ado (MnO <sub>2</sub> /p-PTL)	0.08	1.77 V @ 2 A cm <sup>-2</sup>	2500 h @ 1.8 A cm <sup>-2</sup>	[2]
Ir/Ti <sub>3</sub> O	0.3	1.77 V @ 2 A cm <sup>-2</sup>	700 h @ 1 A cm <sup>-2</sup>	[3]
Ir/TiO <sub>x</sub> @Ti	0.3	1.77 V @ 2 A cm <sup>-2</sup>	400 h @ 2 A cm <sup>-2</sup>	[4]
IrO <sub>2</sub> (101)	1.5	1.78 V @ 2 A cm <sup>-2</sup>	10000 h @ 1.5 A cm <sup>-2</sup>	[5]
Ir@IrO <sub>x</sub> /m-Nb-TiO <sub>2</sub>	0.27	1.72 V @ 2 A cm <sup>-2</sup>	3000 h @ 2 A cm <sup>-2</sup>	[6]
LaIr-Co <sub>3</sub> O <sub>4</sub>	0.2	1.61 V @ 1 A cm <sup>-2</sup>	1000 h @ 1 A cm <sup>-2</sup>	[7]
Ir/TiN	0.1	1.80 V @ 2A cm <sup>-2</sup>	500 h @ 1 A cm <sup>-2</sup>	[8]
DA_IrO <sub>x</sub> /TiO <sub>2</sub>	0.3	1.82 V @ 3A cm <sup>-2</sup>	100 h @ 2 A cm <sup>-2</sup>	[9]
Ir-LiCoO <sub>2</sub>	0.5	1.64 V @ 1 A cm <sup>-2</sup>	150 h @ 1 A cm <sup>-2</sup>	[10]

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