

Supplementary Information

Preparation and characterization of nanostructured Fe-doped CoTe₂ electrocatalysts for the oxygen evolution reaction

Zhi Yang,^{†,a,b} Hao Tan^{†,a} Yu Qi,^a Shiyu Ma,^a Jilin Bai,^a Lifeng Liu^c and Dehua Xiong^{*,a}

^a State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, P. R. China.

^b Department of Materials Science, Fudan University, Shanghai 200433, P. R. China.

^c Songshan Lake Materials Laboratory, Dongguan, 523808, P. R. China.

† Zhi Y. and Hao T. contributed equally in this work.

Email: xiongdehua2010@gmail.com (D. Xiong)

Experimental details:

Reagents

All chemicals used in the experiments including sodium tellurite (Na_2TeO_3), Iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), and Potassium hydroxide (KOH) are of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water was used throughout the study.

Hydrothermal synthesis of Fe-doped CoTe_2

Firstly, to remove the oxide layer and impurities from the bare Co foam surface, the Co foam with a thickness of 1.00 mm was divided into small pieces of size $3.00 \times 4.00 \text{ cm}^2$ and placed in 1.0 M HCl solution for 30 min. Then, the Co foam was cleaned in deionized water (DI) and alcohol in sequence and finally dried at $60 \text{ }^\circ\text{C}$ in vacuum for 30 min. During the hydrothermal experiment, 0.444 g of sodium tellurite (Na_2TeO_3) was added to 65.00 ml of DI water and the solution placed on a magnetic stirrer at room temperature with continuous stirring for 30 min. Afterwards, a certain amount of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.10 g, 0.20 g, 0.30 g, or 0.40 g) was added to the above solution, and magnetic stirring was kept continuously for 30 min to obtain a good mixture. Finally, 5.00 ml of hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was added to the solution, followed by continuous stirring to form a homogeneous solution. Subsequently, the mixed solution was transferred to a 100 ml polytetrafluoroethylene hydrothermal reactor, and the cleaned Co foam was put into the solution in the autoclave reactor.

The above solution in the autoclave reactor was then heated to $200 \text{ }^\circ\text{C}$ (samples denoted as $\text{Co}@0.1\text{gFeCoTe}_2\text{-}200$, $\text{Co}@0.2\text{gFeCoTe}_2\text{-}200$, $\text{Co}@0.3\text{gFeCoTe}_2\text{-}200$, and $\text{Co}@0.4\text{gFeCoTe}_2\text{-}200$) in an oven and kept for 20 h to allow for a complete reaction. After that, the reactor was cooled down to room temperature, and the reacted Co foam was cleaned with anhydrous ethanol (ET) and pure water by ultrasonication for 10 min and then dried in an oven at $50 \text{ }^\circ\text{C}$ for 6 h to obtain the $\text{Co}@\text{FeCoTe}_2\text{-}200$ catalyst electrode. In addition, different hydrothermal reaction temperatures were adopted in this experiment ($180 \text{ }^\circ\text{C}$, $200 \text{ }^\circ\text{C}$, $220 \text{ }^\circ\text{C}$, and $240 \text{ }^\circ\text{C}$). Blank controls were also prepared for the experiments, which were a $\text{Co}@\text{CoTe}_2$ sample without Fe doping

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(denoted as Co@CoTe₂-200) at otherwise the same condition and a piece of bare Co foam (denoted as “bare Co”).

Structural characterization

The crystalline structure was identified by X-ray diffractometry (XRD, Bruker, Germany, D8 DISCOVER) using Co K α radiation ($\lambda = 1.79021 \text{ \AA}$) and a PIXcel detector. The morphology, microstructure, and chemical composition of the products were determined by field-emission scanning electron microscopy (SEM, Zeiss sigma300, Zeiss) and transmission electron microscopy (TEM, FEI Tecnai G2, FEI, USA) equipped with energy-dispersive X-ray spectroscopy (EDS). The composition and surface chemical state of the elements in the samples were investigated by X-ray photoelectron spectrometry (XPS, Thermo Escalab 250Xi, Thermo Fisher Scientific, USA).

Electrochemical measurements

The electrochemical measurements, including cyclic voltammetry (CV), chronopotentiometry (CP), and electrochemical impedance spectroscopy (EIS), were performed by the electrochemical workstation of the CS2350H (Wuhan Corrtest Instruments Corp., China) in 1.0 M KOH solution (pH = 13.50) at room temperature (~25°C). A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes. In detail, CV tests were recorded in the range of 1.05 V to 1.80 V vs. reversible hydrogen electrode (RHE) with a scan rate of 5 mV s⁻¹. To measure the electrochemical active area, CV curves were acquired in the non-Faraday region (-0.05 - 0.05 V vs. SCE) at different scan rates (10, 20, 40, 60, 80, and 100 mV s⁻¹) and fitted to obtain the electrochemical double layer capacitance (C_{dl}). As an effective method to characterize the chemical reaction rate on the electrode surface, electrochemical impedance spectroscopy (EIS) was performed at a constant potential of 1.60 V vs. RHE in the frequency range of 10 mHz - 100 kHz. The EIS data were fitted according to an equivalent circuit diagram consisting of a Randles model, which reflects the charge transfer resistance by its semicircle in the low frequency region. In this experiment, all CV curves were corrected with the iR drop (85%) according to the

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following formula:

$$E_c = E_m - iR_s \quad (S1)$$

where E_m is the potential obtained from the experiment, R_s is the equivalent series resistance obtained by fitting the EIS data, and E_c is the iR-corrected potential. Unless otherwise specified, all the potentials tested versus SCE are converted to those on the RHE scale according to the following formula:

$$E(RHE) = E(SCE) + 0.059 \times pH + 0.241 \quad (S2)$$

Supplementary figures:

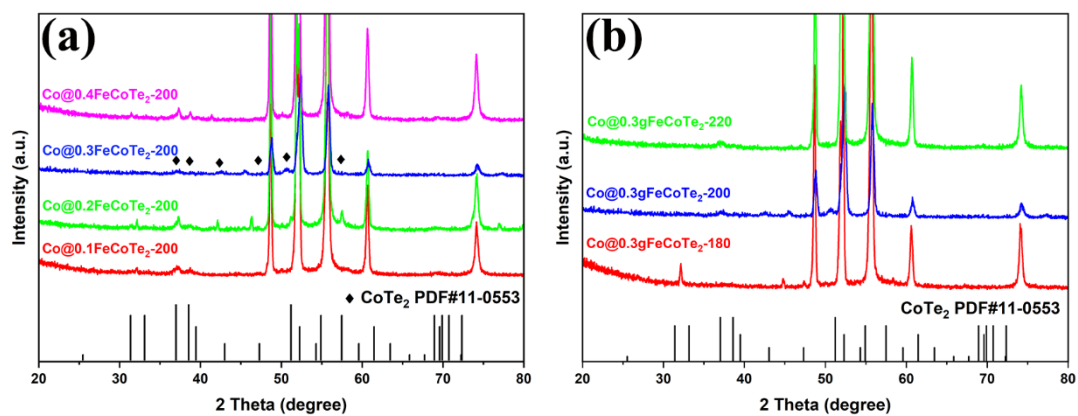


Fig. S1 XRD patterns of Fe-doped cobalt telluride samples with different Fe dopants (a) and at different reaction temperatures (b). The standard powder diffraction pattern of CoTe₂ (JCPDF 11-0553) is given for reference.

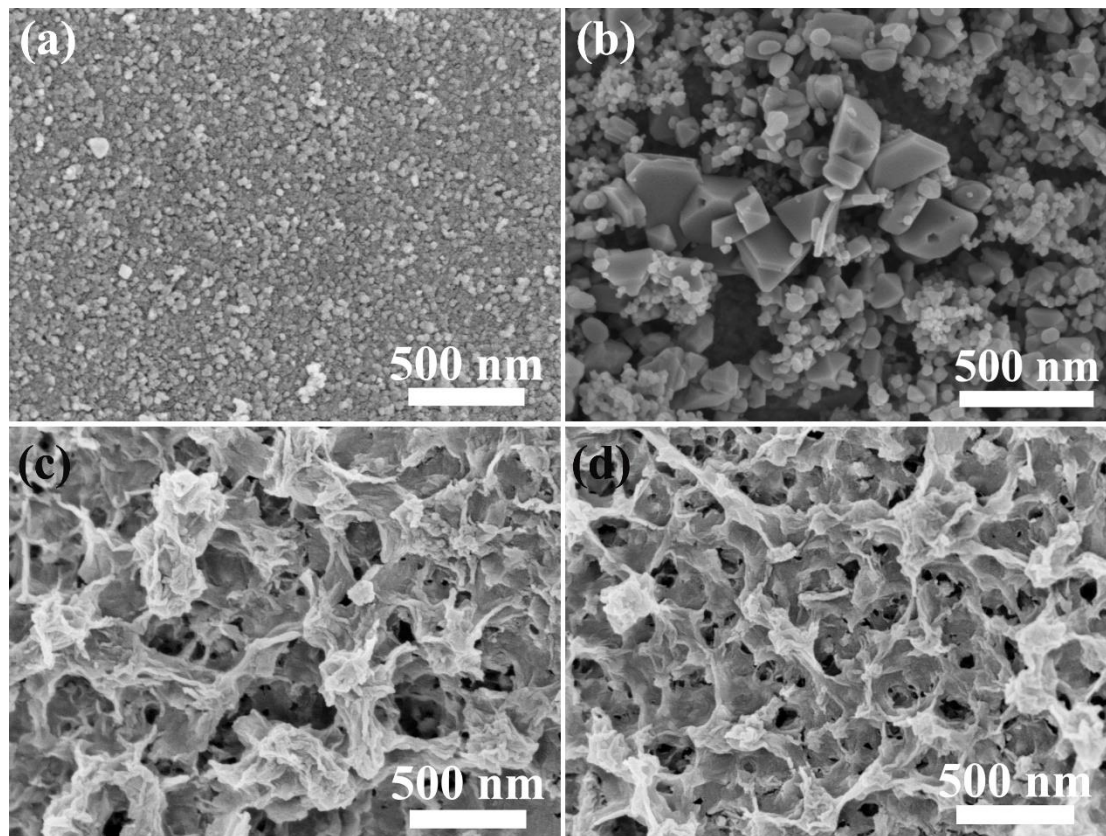


Fig. S2 SEM images of Fe-doped cobalt telluride samples with different Fe dopants, (a) $\text{Co}@0.1\text{gFeCoTe}_2\text{-200}$, (b) $\text{Co}@0.2\text{gFeCoTe}_2\text{-200}$, (c) $\text{Co}@0.3\text{gFeCoTe}_2\text{-200}$, and (d) $\text{Co}@0.4\text{gFeCoTe}_2\text{-200}$.

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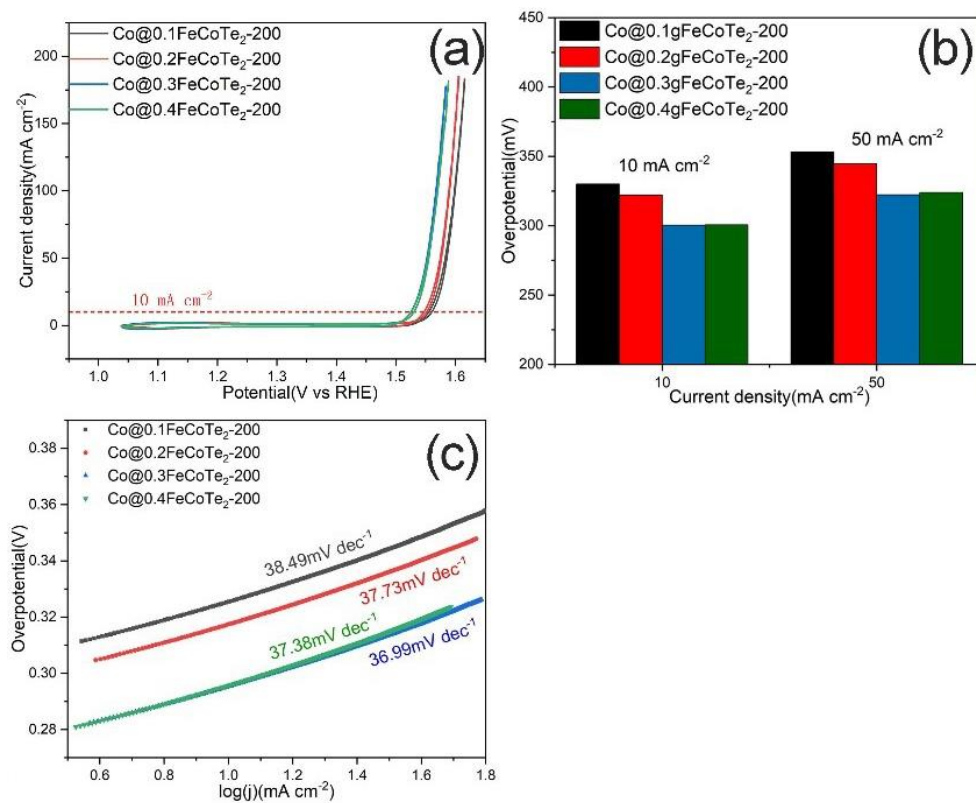


Fig. S3 (a) CV curves, (b) the required overpotential to reach different anodic current densities, (c) Tafel plots of Co@0.1gFeCoTe₂-200, Co@0.2gFeCoTe₂-200, Co@0.3gFeCoTe₂-200, and Co@0.4gFeCoTe₂-200 electrodes.

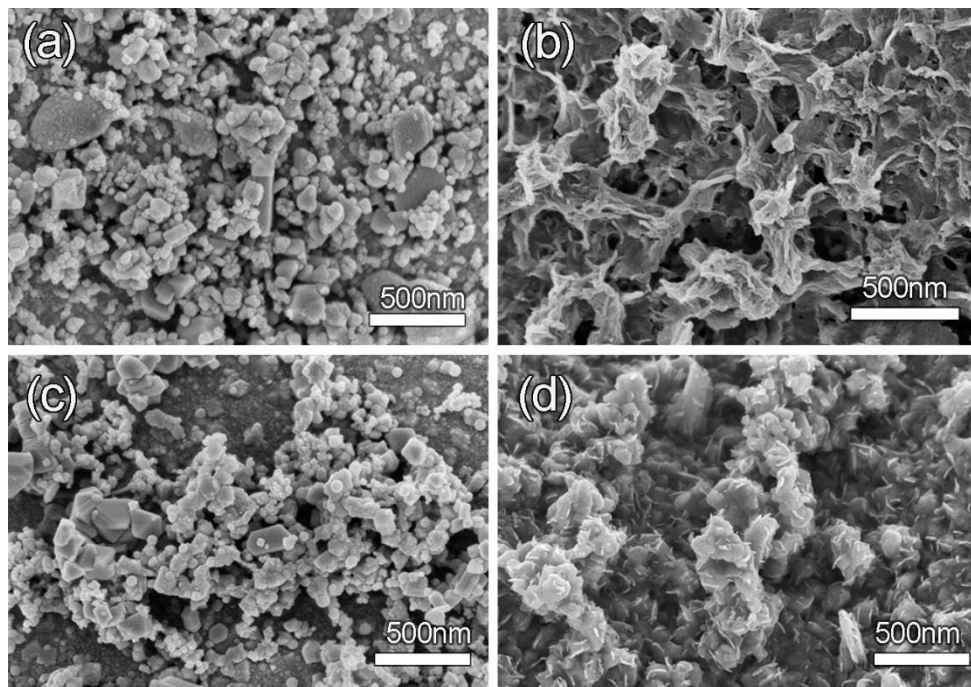


Fig. S4 SEM images of Fe-doped cobalt telluride samples with different reaction temperatures, (a) $\text{Co}@0.3\text{gFeCoTe}_2\text{-180}$, (b) $\text{Co}@0.3\text{gFeCoTe}_2\text{-200}$, (c) $\text{Co}@0.3\text{gFeCoTe}_2\text{-220}$, and (d) $\text{Co}@0.3\text{gFeCoTe}_2\text{-240}$.

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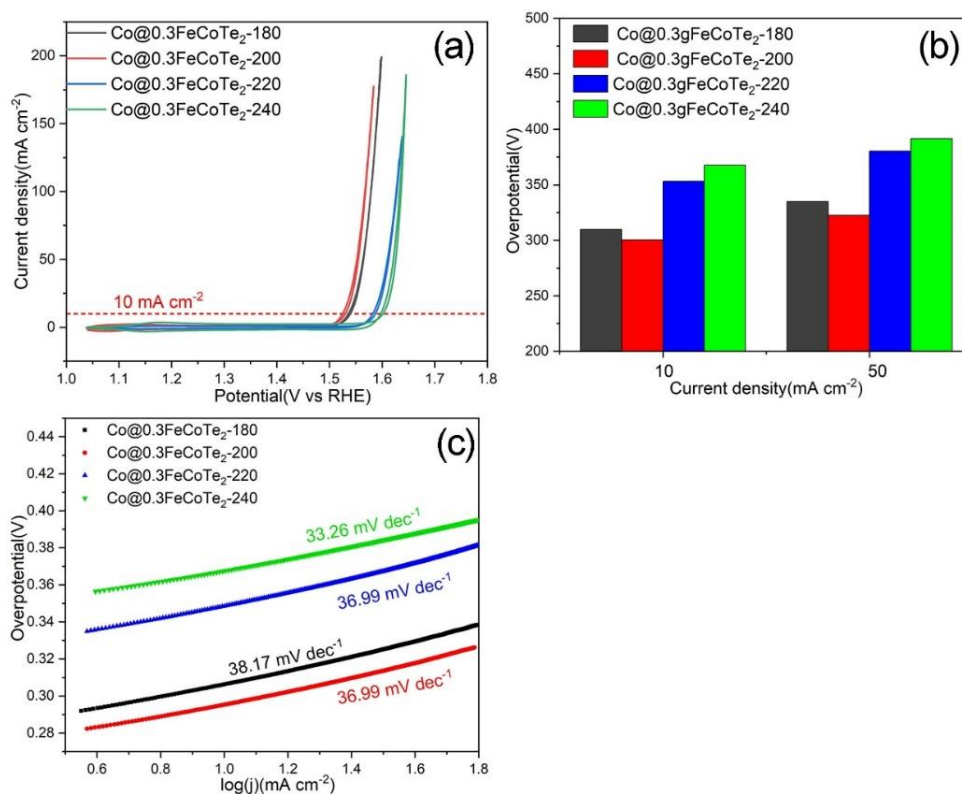


Fig. S5 (a) CV curves, (b) the required overpotential to reach different anodic current densities, (c) Tafel plots of Co@0.3gFeCoTe₂-180, Co@0.3gFeCoTe₂-200, Co@0.3gFeCoTe₂-220, and Co@0.3gFeCoTe₂-240 electrodes.

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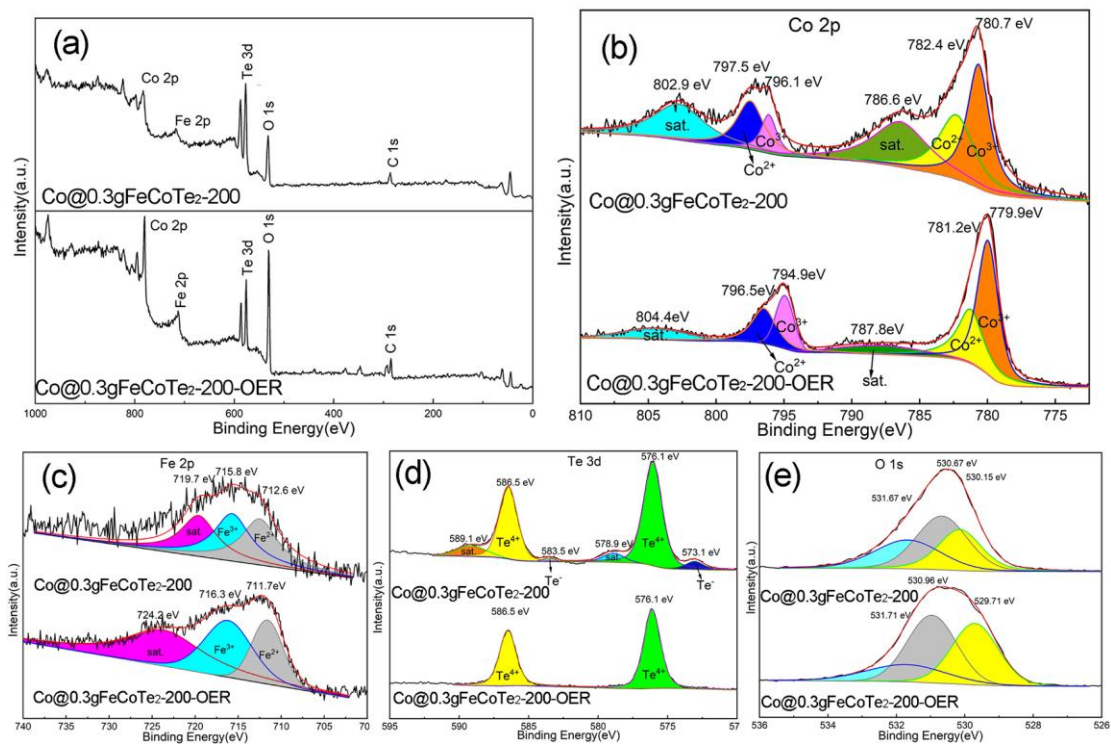


Fig. S6 (a) Survey XPS spectrum, high-resolution spectrum of (b) Co 2p, (c) Fe 2p, (d) Te 3d, and (e) O 1s for the Co@0.3gFeCoTe₂-200 electrode before and after 18 hours of continuous chronopotentiometry tests.

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Table S1. Comparison of the OER performance of Co@0.3gFeCoTe₂-200 electrodes to that of other cobalt based OER catalysts reported recently in the literature.

Catalyst electrodes	Electrolyte	Overpotential (η_{10} /mV)	Tafel Slope (mV dec ⁻¹)	References
Co@0.3gFeCoTe ₂ -200	1.0 M KOH	300	36.99	<i>This work</i>
Co@CoTe ₂ -200		389	46.56	
Bare Co foam		467	65.29	
Fe-Mo/Te-2	1.0 M KOH	300	45.6	<i>Chemical Engineering Journal</i> , 423(2021), 130168.
CoTe ₂ @NCNTFs	1.0 M KOH	330	82.3	<i>J. Mater. Chem. A</i> , 6 (2018), 3684-3691.
Fe-Co _{1.11} Te ₂ @NCNTF-2	1.0 M KOH	297	91	<i>ChemSusChem</i> , 13(2020), 5239-5247.
Fe-CoTe-2	1.0 M KOH	300	45	<i>Electrochimica Acta</i> , 321(2019), 134656.
Ni _{0.81} Fe _{0.19} O	0.5 M KOH	310	25	<i>Nanoscale</i> , 9(2017), 15070-15082.
Co@Co ₉ S ₈ -180	0.1 M KOH	350	41	<i>Chem.-Eur. J.</i> , 23(2017) 8749-8755.
RuCoS ₂ /CC	1.0 M KOH	315	74	<i>Journal of Industrial and Engineering Chemistry</i> , 113(2022), 316-324.
Co _{0.63} Te	1.0 M KOH	317	52	<i>Sustainable Energy Fuels</i> , 6(2022), 4146-4152
CuFe ₂ O ₄	1.0 M KOH	369	76.3	<i>Adv. Powder Technol.</i> , 33(2022), 10.
NiFe ₂ O ₄		386	85.7	
CoFe ₂ O ₄		448	148.1	