

**Fe incorporation-induced electronic modification of Co-tannic acid complex nanoflowers for high-performance water oxidation**

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## Experimental section

### 1. Reagents and chemicals

Tannic acid (TA), NaOH,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were supplied by Aladdin Chemistry Co., Ltd (Shanghai, China). Commercial  $\text{RuO}_2$  was purchased from Johnson Matthey Chemicals Ltd (Shanghai, China). All reagents were of analytical reagent grade and used without further purification.

### 2. Synthesis of $\text{Fe}_{0.15}\text{Co}_{0.85}\text{-TA}$

In a typical synthesis, 8.5 g of tannic acid was firstly dispersed into NaOH solution under constant stirring to obtain  $0.02 \text{ mol L}^{-1}$  sodium tannate solution. Subsequently, 4.2 mmol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 1.4 mmol of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added into 35 mL of the above sodium tannate solution with vigorous stirring for 30 min. Afterwards, the resultant solution was transferred into a 50 mL stainless Teflon-lined autoclave and heated at  $120 \text{ }^\circ\text{C}$  for 6 h. Finally, the  $\text{Fe}_{0.15}\text{Co}_{0.85}\text{-TA}$  sample was obtained by centrifugation, washed with water and absolute ethanol for several times and dried at  $40 \text{ }^\circ\text{C}$  for 12 h. For comparison,  $\text{Fe}_{0.1}\text{Co}_{0.9}\text{-TA}$ ,  $\text{Fe}_{0.24}\text{Co}_{0.76}\text{-TA}$ , Fe-TA and Co-TA samples were also synthesized under the identical synthetic procedure except varying the Co/Fe feeding mole ratios of 4/1, 3/1, 2/1, 1/0, and 0/1, respectively.

### 3. Physicochemical characterizations

The morphology and structure of samples were examined by transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV) and scanning electron microscopy (SEM, Hitachi S-4800). The crystallinity of the products was analyzed by X-ray diffraction (XRD) patterns on a Model D/max-rC X-ray diffractometer with a  $\text{Cu K}\alpha$

radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). The surface chemistry state of samples was identified by X-ray photoelectron spectroscopy (XPS) using a Thermo VG Scientific ESCALAB 250 spectrometer with an Al K $\alpha$  radiator. The BET specific surface area was measured at 77 K on a Micromeritics ASAP 2050 system. Raman spectrum was recorded on a Raman spectrometer (LabRAMHR800,  $\lambda = 514 \text{ nm}$ ). FT-IR spectroscopy was carried out with a Nicolet 520 SXFTIR spectrometer. The electron spin resonance (ESR) test were conducted using an ECS 106 ESR spectrometer (Bruker, Rheinstetten, Germany) with an X-band resonator (ER 4103TM). All ICP measurements were carried out on an IRIS Intrepid instrument (Thermo Fisher, USA).

#### 4. *Electrochemical measurement*

All electrochemical tests were performed on a CHI 760E electrochemical workstation in 1.0 M KOH solution using a standard three-electrode system with a glassy carbon electrode (GCE) as working electrode, a graphite rod as counter electrode, and a saturated calomel reference electrode (SCE) as the reference electrode. For the preparation of the working electrode, 5 mg of the as-synthesized Fe<sub>x</sub>Co<sub>1-x</sub>-TA family catalysts were dispersed into 1 mL of ethanol solution (the volume ratio of ethanol to water is 1:3) for at least 30 min under ultrasonication to form a catalyst ink. Then, 8  $\mu\text{L}$  of the obtained ink was dropped on the surface of polished GCE and then dried at 40 °C. Subsequently, 4  $\mu\text{L}$  of Nafion (5 wt.%, Sigma-Aldrich) was dropped on the surface of catalysts modified GCE and then dried before electrochemical test. Linear sweep voltammetry (LSV) were carried out with a scan rate of 5 mV s<sup>-1</sup> and manually *iR*-corrected. The electrochemical double-layer capacitances ( $C_{dl}$ ) were determined by

a series of CV tests obtained in the non-Faradaic region (1.02 - 1.12 V) at different scan rates (20 - 100 mV s<sup>-1</sup>). The stability measurements were investigated by the chronoamperometry test performed at a constant potential of 1.5 V and the continuous CV scanning 2000 cycles at a scan rate of 0.1 V s<sup>-1</sup>. In this work, all potentials were calibrated to reversible hydrogen electrode (RHE). The equation of potential conversion from SCE to RHE was described as follows:  $E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \text{ pH} + 0.242$ .

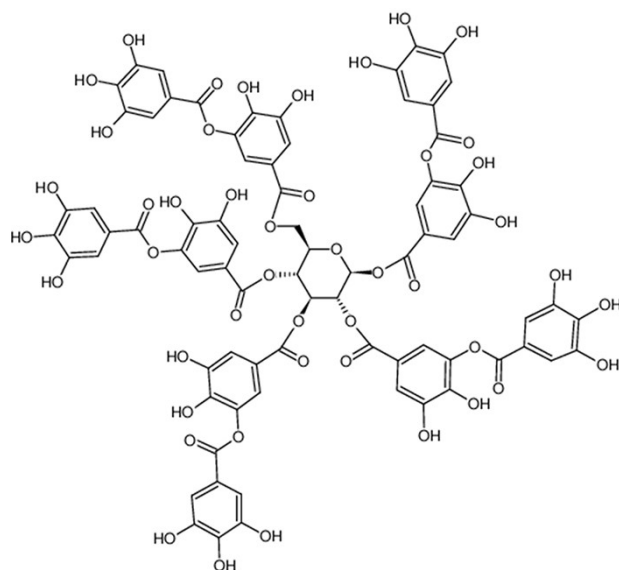


Figure S1 The molecule structure of tannic acid (TA).

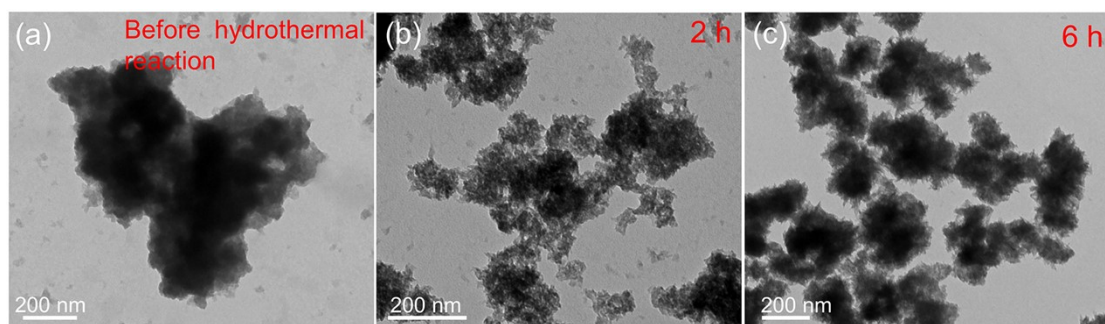


Figure S2 TEM images of Fe<sub>0.15</sub>Co<sub>0.85</sub>-TA intermediates collected at different reaction time: (a) before hydrothermal reaction, (b) 2 h and (c) 6 h.

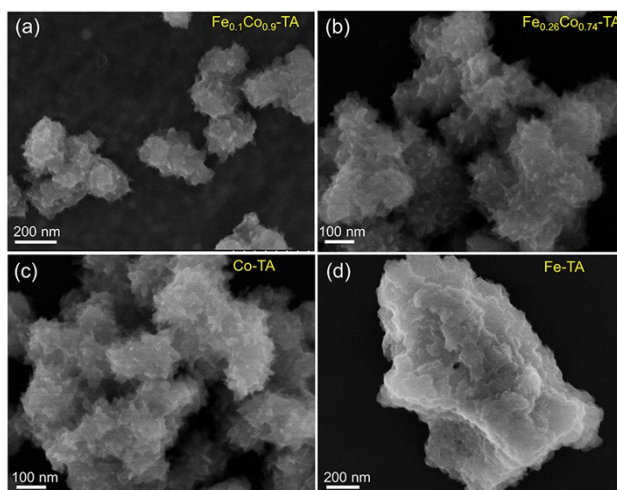


Figure S3 SEM images of different contrastive samples. (a) Fe<sub>0.1</sub>Co<sub>0.9</sub>-TA, (b) Fe<sub>0.24</sub>Co<sub>0.76</sub>-TA, (c) Co-TA and (d) Fe-TA.

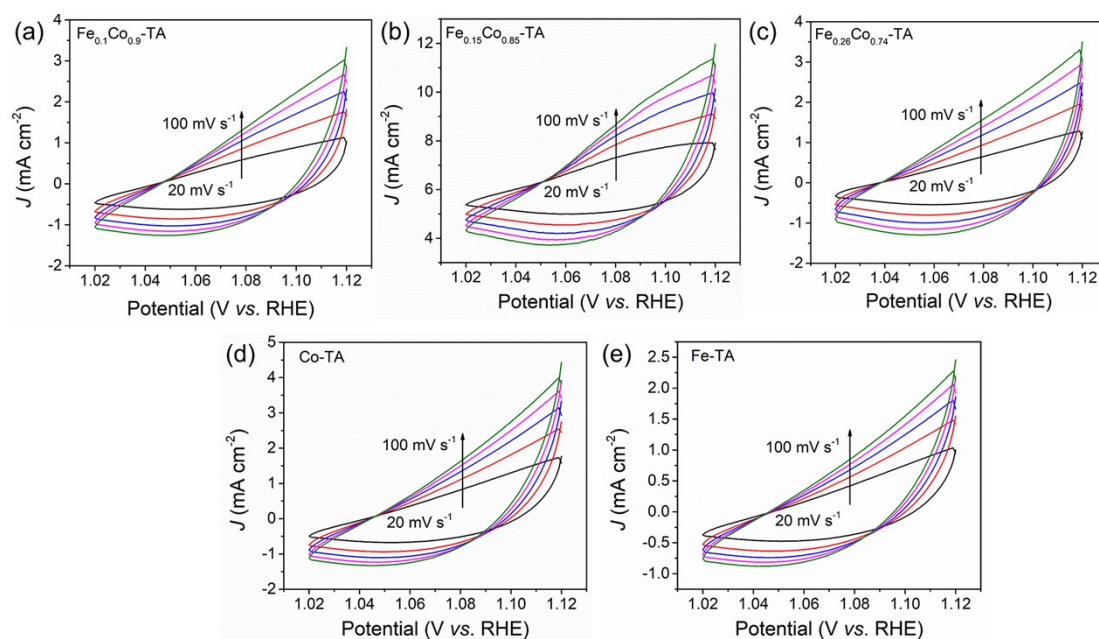


Figure S4 CV curves of the synthesized Fe<sub>x</sub>Co<sub>(1-x)</sub>-TA catalysts in the non-Faradaic region (1.02 – 1.12 V) obtained at different scanning rates. (a) Fe<sub>0.1</sub>Co<sub>0.9</sub>-TA, (b) Fe<sub>0.15</sub>Co<sub>0.85</sub>-TA, (c) Fe<sub>0.24</sub>Co<sub>0.76</sub>-TA, (d) Co-TA and (e) Fe-TA.

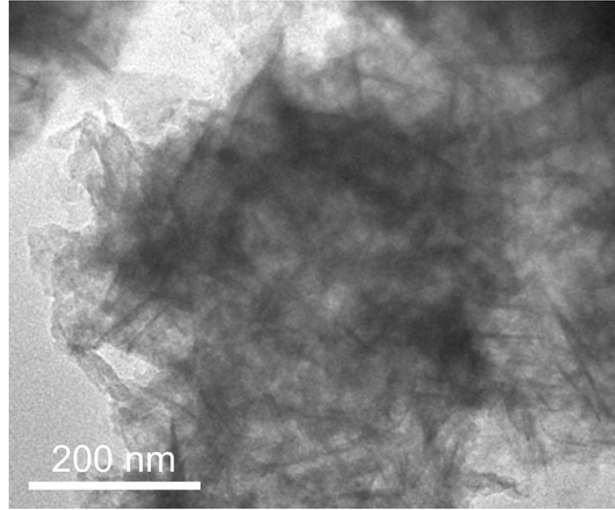


Figure S5 TEM image of the Fe<sub>0.15</sub>Co<sub>0.85</sub>-TA after OER test.

Table S1 Determinations of the content of Fe and Co in  $\text{Fe}_x\text{Co}_{(1-x)}\text{-TA}$  by ICP-OES.

Feed mole ratios (Co/Fe)	Co (at. %) in $\text{Fe}_x\text{Co}_{(1-x)}\text{-TA}$	Fe (at. %) in $\text{Fe}_x\text{Co}_{(1-x)}\text{-TA}$
4/1	0.90	0.10
3/1	0.85	0.15
2/1	0.74	0.26



Table S2 Comparison of OER performance of Fe<sub>0.15</sub>Co<sub>0.85</sub>-TA nanoflowers with some previously reported Co-based catalysts in 1.0 M KOH solution.

Catalysts	Overpotential at 10 mA cm <sup>-2</sup> (mV)	Tafel slope (mV dec <sup>-1</sup> )	References
<b>Fe<sub>0.15</sub>Co<sub>0.85</sub>-TA nanoflowers</b>	<b>272</b>	<b>53.9</b>	<b>This work</b>
NPMC/CoFe	310	50.6	<i>J. Power Sources</i> , 2019, 441, 227177.
Co <sub>3</sub> O <sub>4</sub> -CNTs	370	87	<i>Appl. Surf. Sci.</i> , 2019, 497, 143818.
CoFe@NiFe-200/NF	190	45.71	<i>Appl. Catal. B: Environ.</i> , 2019, 253, 131.
IrClx-Co(OH) <sub>2</sub> /CNTs	230	71.64	<i>Appl. Catal. B: Environ.</i> , 2020, 279, 119398.
N-NiCoPx/NCF	298	60	<i>Chem. Eng. J.</i> , 2020, 402, 126257.
Fe-CoNi-OH	210	28	<i>Chem. Eng. J.</i> , 2021, 403, 126304.
Co <sub>0.8</sub> Fe <sub>0.2</sub> P	240	55	<i>ACS Appl. Mater. Interfaces</i> , 2020, 12, 46578.
(Fe,Co)SPPc-900-sp	353	53	<i>ACS Sustainable Chem. Eng.</i> , 2020, 8, 13147.
Fe-Co <sub>3</sub> O <sub>4</sub>	262	43	<i>Adv. Mater.</i> , 2020, 32, 2002235.
Ni-Co-P/GDY	290	72.7	<i>ChemCatChem</i> 2019, 11, 5407.
Co@LCO-NFs	270	43	<i>J. Mater. Chem. A</i> , 2020, 8, 19946.
CoFe@NC-700	470	135.7	<i>Mater. Res. Express</i> , 2020, 7, 085002.
Co/N-CNTs	310	66	<i>Small</i> , 2020, 16, 2002427.
Co <sub>9</sub> S <sub>8</sub>	288	79	<i>J. Mater. Chem. A</i> , 2018, 6, 7592.
CoS <sub>2</sub> HNSs	290	57	<i>Nanoscale</i> , 2018, 10, 4816.
Fe-SAs/Fe <sub>3</sub> C-Fe@NC	340	43	<i>Small</i> , 2020, 16, 1906057.
Co@Co <sub>3</sub> O <sub>4</sub> /N-C	390	88	<i>Chem. Commun.</i> , 2018, 54, 12746.