**Supporting Information**

**Oxygen vacancy on Nb2O5 enhanced the performance of H2O2 electrosynthesis from O2 reduction**

Xiaoge Peng,‡ Shijie Zhang,‡ Zhikang Bao, Lei Ding, Guoliang Wang, Yizhen Shao, Zaixiang Xu, Wenkai Ji, Ge Feng, Shibin Wang, Xing Zhong, Jianguo Wang\*

a. Institute of Industrial Catalysis, College of Chemical Engineering, State Key Laboratory Breeding Base of Green-Chemical Synthesis

Technology, Zhejiang University of Technology, Hangzhou 310032, Zhejiang, China.

‡ X.G. Peng and S.J. Zhang contribute to this work equally.

**Corresponding Author**

jgw@zjut.edu.cn (Jianguo Wang).

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2. Experimental section

1. Materials Synthesis

Niobium Pentoxide (Nb2O5, Macklin, AR 99.9%), Nafion solution (DuPont), Cerium Sulfate (Ce(SO4)2, Aladdin, AR 98%), sulfuric acid (H2SO4, Lingfeng Chemical Reagent Co., Ltd, AR 99.9%), Potassium hydroxide (KOH, Sinopharm Chemical Reagent Co., Ltd, AR 99.5%), Ethanol (CH3OH, Sinopharm Chemical Reagent Co., Ltd, AR 99.5%), deionized water (DI, Millipore 18.2 MΩ cm-1), N2 gas (99.99%), H2 gas (99.99%) were used without further purification.

The commercial Nb2O5 powder was heated to 100, 200, 300, 400 and 500 °C at a heating rate of 5 °C min-1 under H2 atmosphere and maintained 2 h. Subsequently, the samples were cooled down to room temperature under N2 atmosphere. The as-fabricated sample was labelled as H-T (T is 100, 200, 300, 400 and 500 °C).

2. Characterization.

Scanning electron microscopy (SEM) inspections were conducted on a Hitachi FE-SEM S-4700 at 15 kV. Transmission electron microscope (TEM) images were conducted by Tecnai G2F30S−Twin operated at 300 kV. Power X-ray diffractometer (XRD) was recorded with a PANalytical X’Pert PRO powder diffractometer using Cu Kα radiation (λ = 0.1541 nm). X-ray photoelectron spectroscopy (XPS) measurement was performed on Thermo Scientific K-Alpha spectrometer with Al Kα radiation (hv = 1486.6 eV), calibration of the binding energies was done using the adventitious C 1 s peak at 284.8 eV. Electron spin resonance (ESR) was performed on Bruker EMX-plus. UV-vis was done on MICROSOLA equipment. Raman spectra was measured with a spectrometer (WITec alpha300R) using 488 nm excitation. photoluminescence (PL) spectroscopy was performed on the FLS980 with an excitation laser at 375 nm in the wavelength range of 400-700 nm at room temperature.

3. Electrochemical Measurements.

The ORR measurement was performed in O2-saturated 0.1 M KOH solution, and the RRDE rotating rate of 1600 rpm. The three-electrode system: the drop-cast is used as the working electrode, the platinum (Pt) wire and saturated calomel electrode (Hg/Hg2Cl2) are used as the counter electrode and reference electrode, respectively. All reported potential is referred to as the reversible hydrogen electrode (RHE), which is calculated using the eq 1:

The performance measurement of ORR was implemented, typically, the as-prepared catalyst (4.0 mg) and 5 wt.% Nafion solution (100 µL) were mixed in 900 µL ethanol solution followed by 0.5 h bath sonication to obtain a homogeneous ink. Then, the 5 µL as-prepared catalyst ink (5 µL) was dropwise to the disk-electrode of the RRDE (0.1256 cm2 glassy carbon (GC) disk area, 0.1884 cm2 Pt ring area) electrode and dried under the heating lamp. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were carried out at the scan rate of 50 mV s-1 and 10 mV s-1, respectively, and O2 flow rate of 30 mL min-1. The H2O2 selectivity and electron transfer number (n) was calculated using the following eq 2 and eq 3, respectively. Where Id is the disk current, Ir is the ring current and N is the collection efficiency.1

The collection efficiency (N) was conducted as follow: 0.1 M KOH and 10 mM K3Fe(CN)6 as electrolyte on a blank RRDE electrode, where Fe3+ to generated Fe2+ on the disk electrode, subsequently was oxidated to Fe3+ on the ring electrode, the process only one-electron reaction to obtain the ring electrode collection efficiency.2 3, 4 Typically, RRDE voltammogram is recorded by performing LSV with different rotation rate (400, 625, 900, 1225, 1600, 2025 and 2500 rpm), and the potential range from 1.2 V to 0 V at the scan rate of 10 mV s-1. Meanwhile, the ring potential is held at 1.30 V. The collection efficiency (N) of RRDE is calculated using the eq 4.2

The corresponding faradaic efficiency of RRDE can be obtained by eq 5:

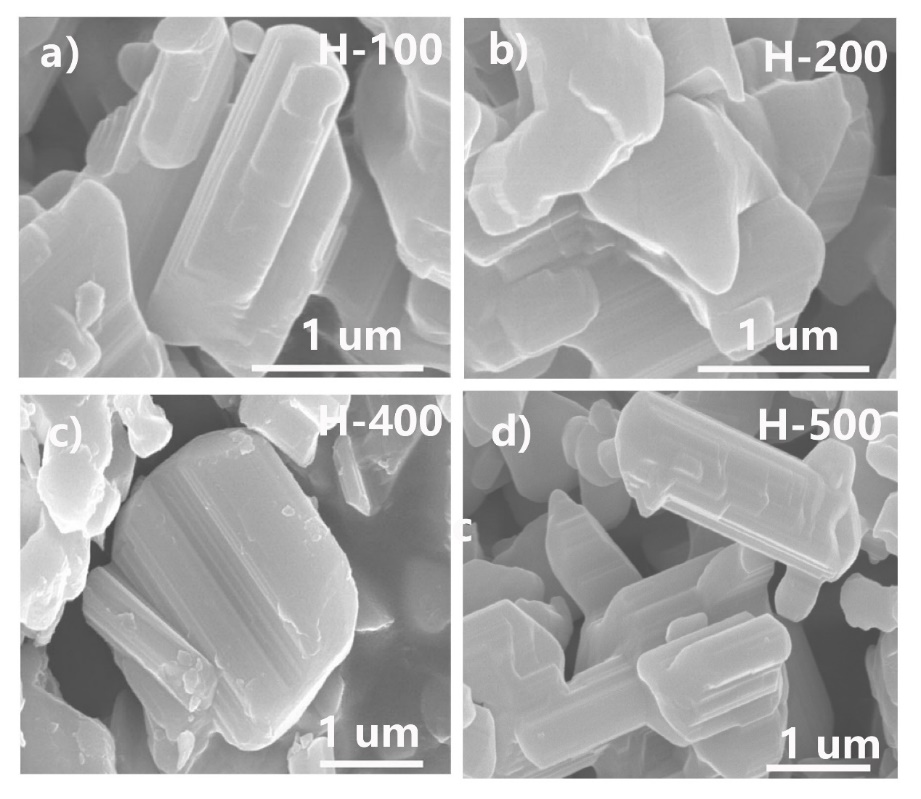
4. The measurement of yield.

The homemade electrolytic cell includes the cathode and anode chamber, the 0.1 M KOH solution as electrolyte and the nafion 117 membrane is clamped between the middle of the two chambers. The hydrophobic gas diffusion layer (GDL) coating the catalyst powers be used the cathode, the anode coated with the Ir-Ta. To improve oxygen utilization, oxygen cavity at the bottom of the cathode chamber was set. The electrocatalyst is loaded on the GDL, where the whole lay out O2.

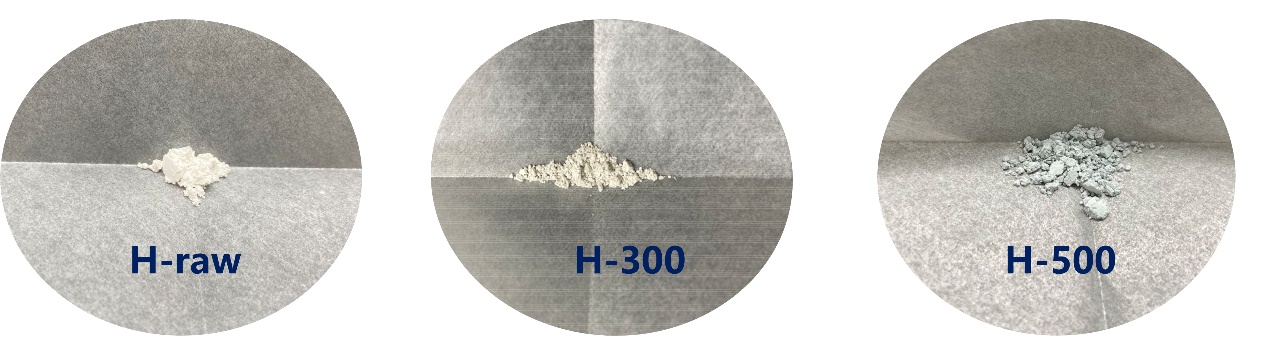
The concentration of H2O2 is determined by a colorimetry.5 Note, the production of H2O2 are accumulated during the ORR process. The detail of this method could be described as follows: As-prepared 50 μL solution was added into the 2 mL 10 Mm (Ce(SO4)2). The yellow Ce4+ is oxidized by H2O2 to colorless Ce3+ (eq 6). Subsequently, absorbance of the mixed solution is measured at UV-vis technology (λ = 316 nm), and the H2O2 concentration is identified by the standard curve.

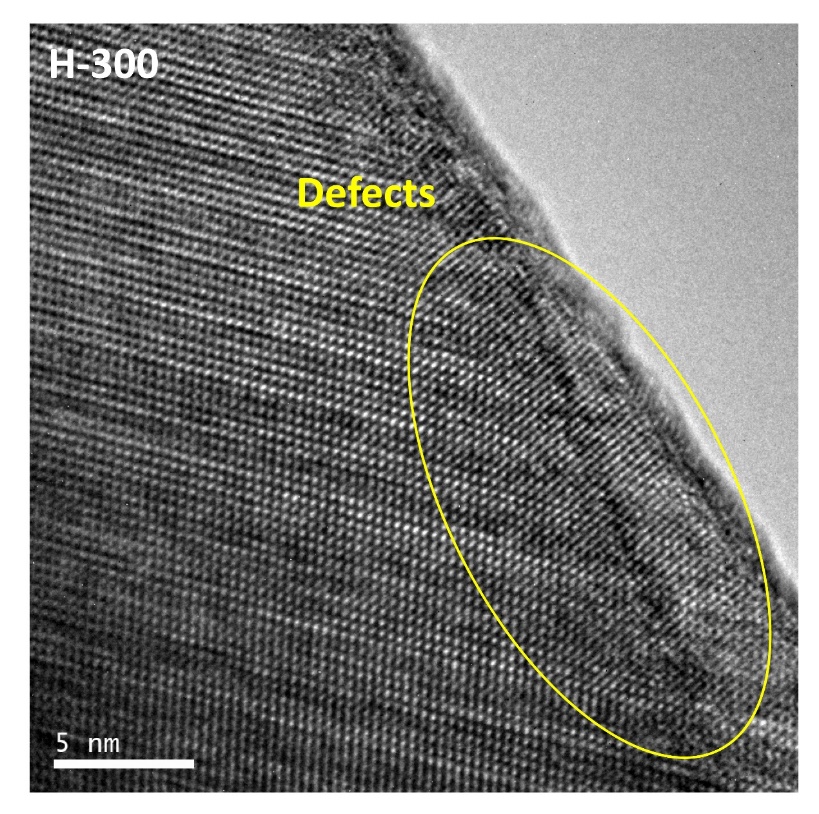
The corresponding faradaic efficiency of H2O2 production can be obtained by eq 7:

where C is the produced H2O2 concentration (mol L-1), V is the volume of electrolyte (L), F is the faraday constant (96485 C mol-1), Q is the passed charge amount (C).

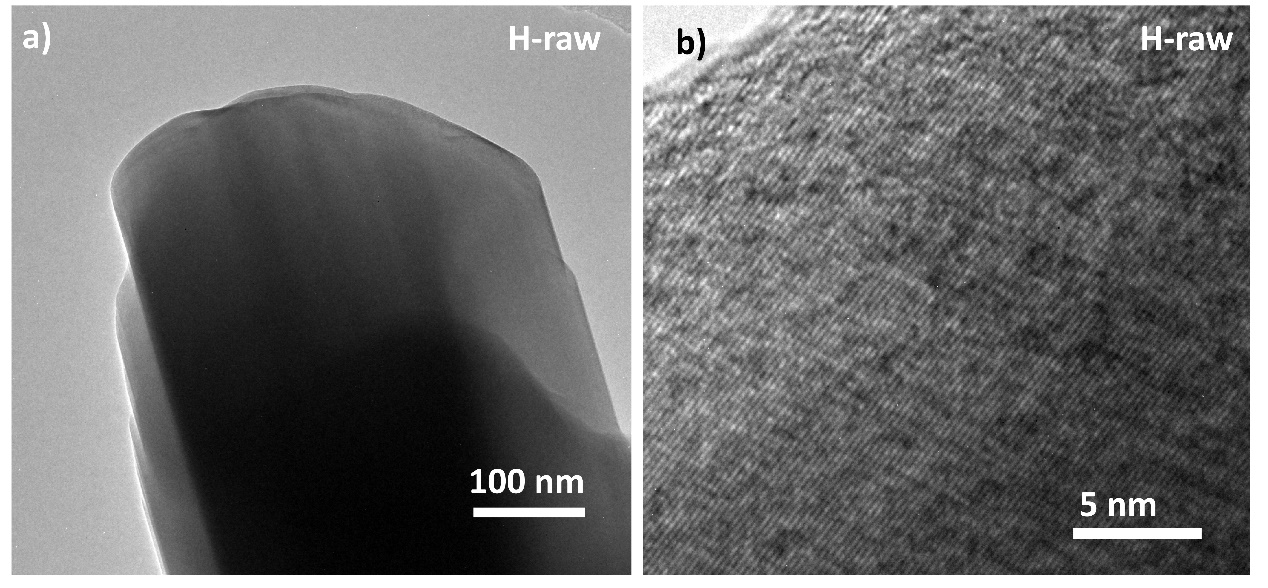
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**Figure S1.** TheSEM images of H-Nb2O5 materials were prepared at different temperatures. a) H-100. b) H-200. c) H-400. d) H-500.

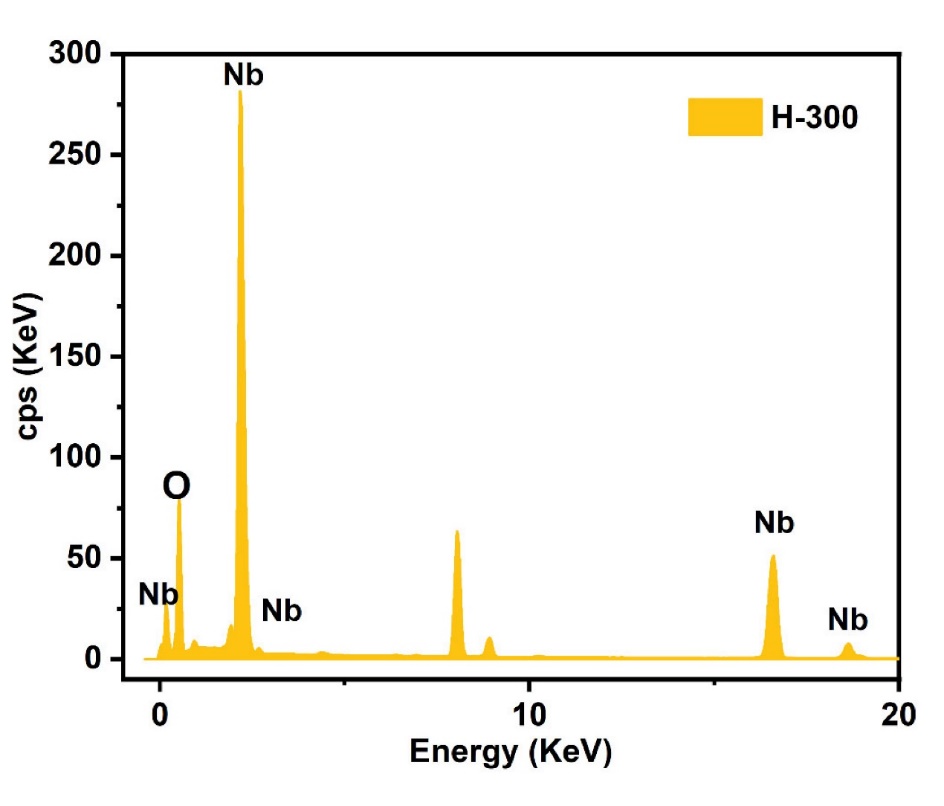
** Figure S2.** Thecatalyst power of Nb2O5 annealing at different temperatures. a) the pristine Nb2O5. b) annealing at 300 °C. c) annealing at 500 °C.

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**Figure S3.** TheTEM images of H-300 material (the yellow circle highlights the disorder area).

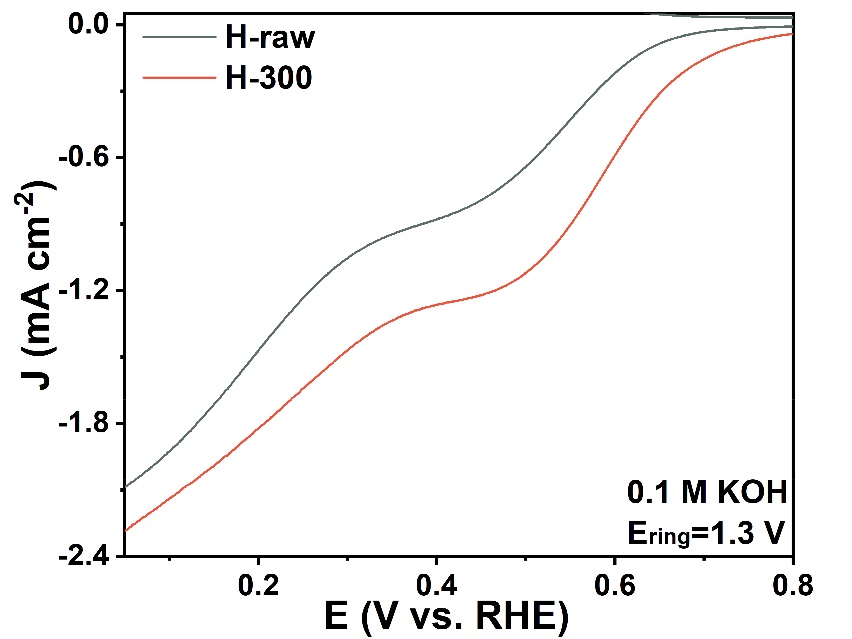
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**Figure S4.** TheTEM images of H-raw. a) at 100 nm. b) at 5 nm.

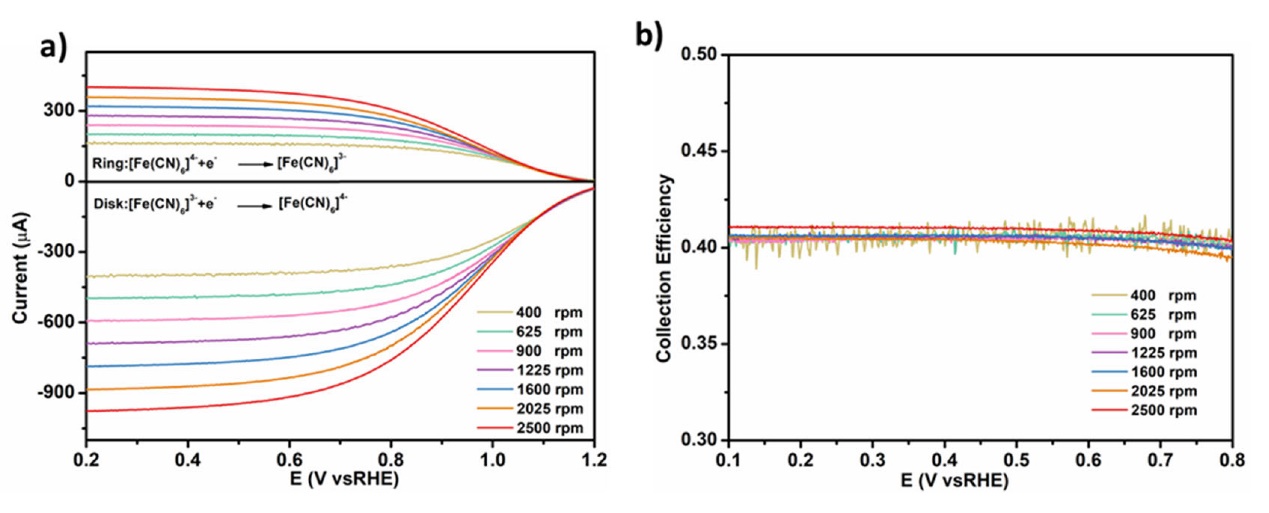
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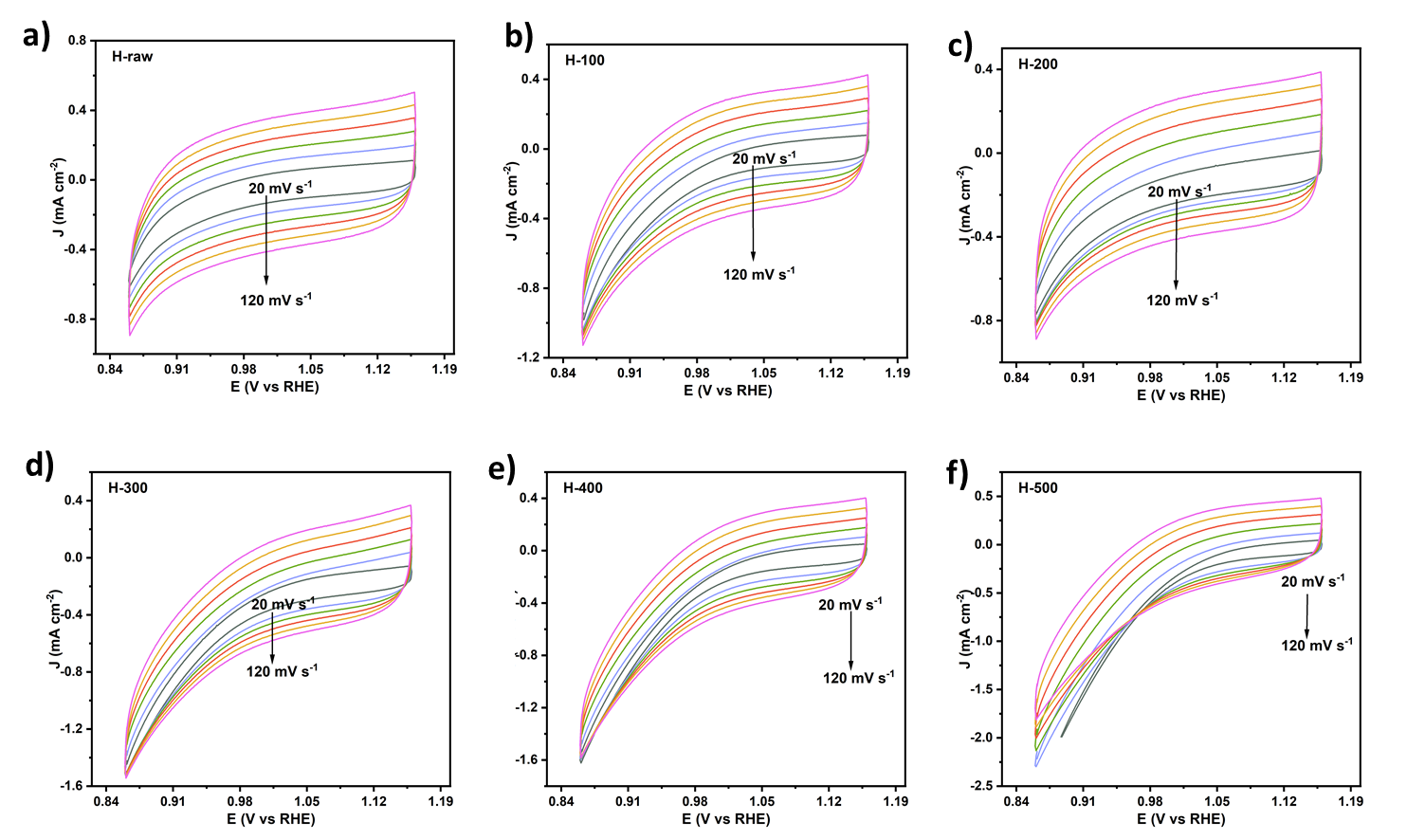
**Figure S5.** The EDS energy spectrum analysis results of H-300.

**Figure S6.** The CV of the H-raw, H-100, H-200, H-400 and H-500.

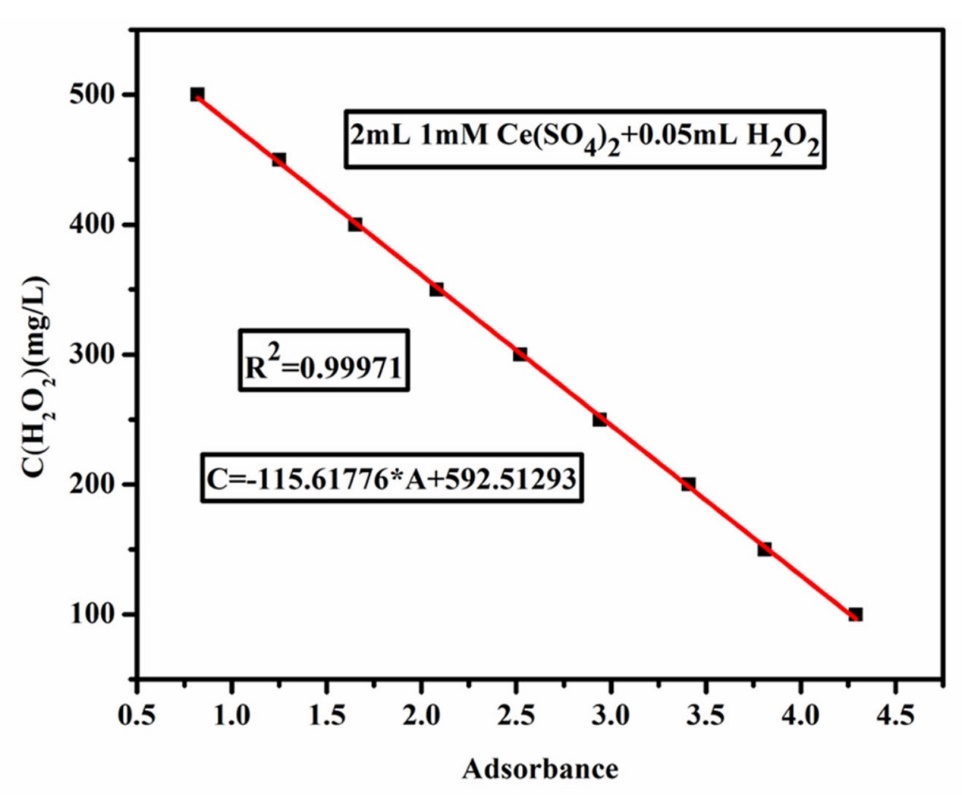


**Figure S7.** The LSV of the H-raw and H-300.

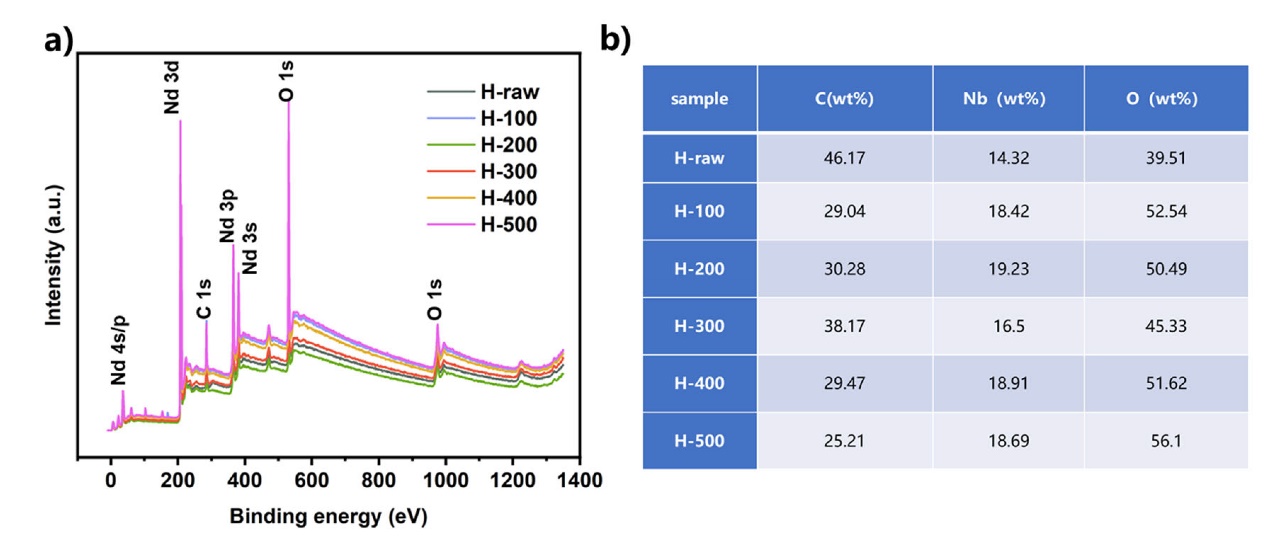
**** **Figure S8.** Measurement of the collection efficiency of the blank RRDE in Ar-saturated 0.1 M KOH dissolved with 10 mM of K3[Fe(CN)6]. a) RRDE voltammograms recorded at different rotation rates by performing LSV on the disk from 1.2 to 0 VRHE at 10 mV/s while holding the ring potential at 1.50 VRHE. b) the corresponding collection efficiency of RRDE voltammograms as a function of the potential. All potentials in this figure are presented without iR-correction.



**Figure S9.** The ECSA analysis of H-T catalysts measured in 0.1 M KOH at different scan rate (20, 40, 60, 80, 100 and 120 mV s-1).

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**Figure S10.** The calibration curve of Ce(SO4)2 solution and the standard curve of its reaction with hydrogen peroxide**.**

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**Figure S11.** The XPS of H-T catalysts Full survey spectra.



**Figure S12.** The Nb 3d XPS spectra of H-T catalysts.

**Figure S13.** The photoluminescence (PL) spectroscope of H-raw, H-300 and H- catalysts.

**Figure S14.** The UV-vis DSR spectroscope of H-raw, H-300 and H- catalysts.

**Reference**

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