

SUPPLEMENTARY MATERIAL

Enhanced performance in the direct electrocatalytic synthesis of ammonia from N₂ and H₂O by an in-situ electrochemical activation of CNT-supported iron oxide nanoparticles

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1. Experimental methods

1a. Cell configuration used for the direct NH₃ electrocatalytic synthesis

The electrocatalytic cell operating at ambient temperature/pressure used for the direct NH₃ synthesis from N₂ and H₂O is shown in **Figure S1**.

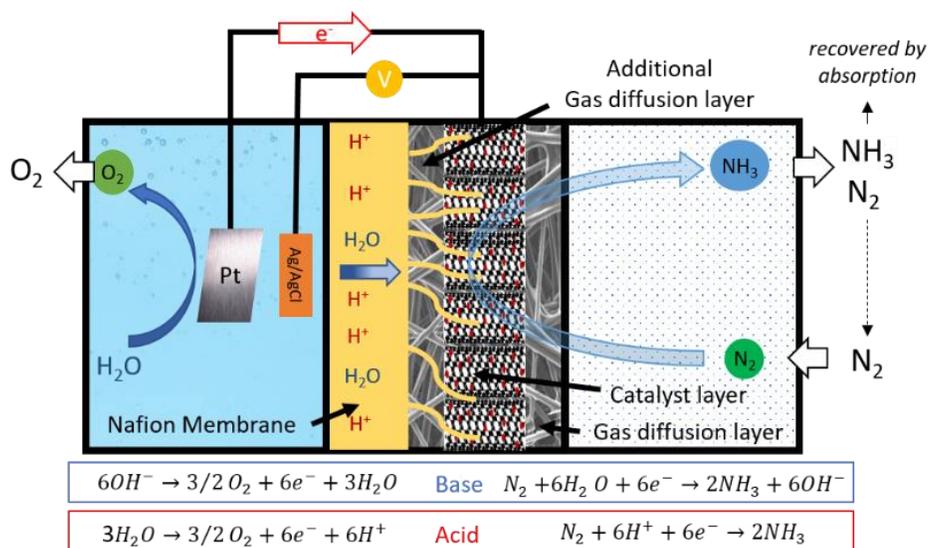


Figure S1. Schematic view of the three-phase reactor for electrochemical ammonia synthesis.

1b. Detection of ammonia

The method used for low ammonia concentration detection was adapted from the standard methods for the examination of water and wastewater.

Ammonia concentration was detected by spectrophotometry with salicylic acid and/or ion selective electrode analysis (Orion™ High-Performance Ammonia Electrode 9512HPBNWP) methods. Initially, two absorbers (in series) were used to probe the ammonia produced. But it was found that all the ammonia was collected by the first absorber and no ammonia was measured in the second absorber. Therefore, only a single absorber was used in the remaining experiments. Ammonia ion selective electrode was used also as alternative, and described below, but found to give lower precision in the estimations, that for the spectrophotometric measurement with salicylic acid was found to be less than 5% in repeated tests.

1b.1 - Ammonia-selective electrode method

Apparatus: Electrometer; ammonia ion selective electrode - ISE (Thermo Scientific Orion high performance ammonia ion selective electrode Cat.No.9512HPBNWP); Magnetic stirrer.

Reagents: Ammonia-free water; Standard ammonium chloride solution: 1000 ppm as NH₄⁺; Ionic Strength Adjuster (ISA).

Procedures

- a. Preparation of ammonia standards: series of standard solutions were prepared with the concentrations of 1, 0.5, 0.1, and 0.05 (as NH_4^+) in 0.001 M H_2SO_4 (absorber).
- b. Electrometer calibration: the following steps were performed during the electrometer calibration:
 1. The electrode was soaked in ammonia electrode storage solution (1 ppm standard with alkaline reagent) for at least 15 min.
 2. The meter measurement mode was changed to mV mode.
 3. 50 mL of each standard was measured into separate, clean beakers. 0.5 mL of alkaline solution was added to each beaker prior to calibration waiting until the reading was stable for 2 minutes.
 4. The mV value and $\lg(\text{ppm})$ were used as Y axis and X axis respectively, to prepare the standard curve.
 5. The Electrode slope was checked (Slope should be between 54 and 60 in a temperature range of 20-25 °C).
- c. 50 mL of sample was measured and 0.5 mL of alkaline solution was added. The measurement was then recorded using ISE (at least 2 minutes are necessary to get stable readings).
- d. Calculation

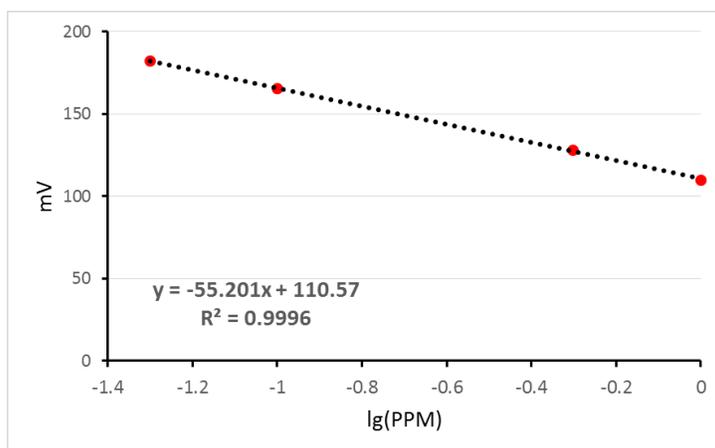


Figure S2. Calibration of NH_3 in 0.001M H_2SO_4 from 0.05 ppm to 1 ppm.

1.b.2 - Spectrophotometry measurement with salicylic acid

Apparatus: A spectrophotometer (Thermo Fischer Evolution 200) was used at fixed wavelength ($\lambda=690$ nm) with a light path of 1 cm.

Reagents used:

1. Coloring solution: sodium salicylate (0.4 M) and sodium hydroxide (0.32 M);
2. Oxidation solution: sodium hypochlorite ($\text{pCl}=4\sim 4.9$) and sodium hydroxide (0.75M);
3. Catalyst solution: 0.1g $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ diluted to 10ml with deionized water.
4. Standard ammonium solution.

Procedure:

4 mL of sample was taken. Then 50 μL of oxidizing solution, 500 μL of coloring solution and 50 μL of catalyst solution were added respectively to the sample solution. Absorbance measurements were performed after 1 hr at $\lambda=690$ nm. The calibration curve below was used to calculate the ammonia concentration.

Calibrations

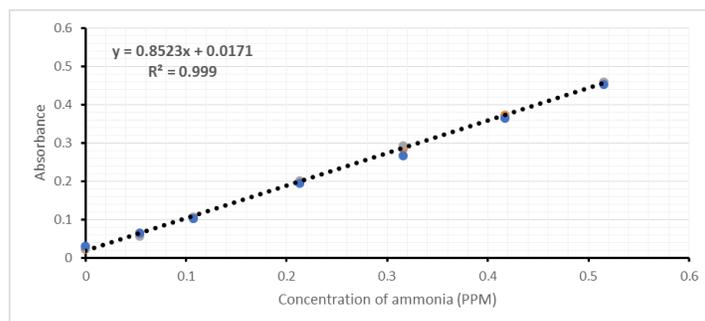


Figure S3. Spectrophotometry with salicylic acid with three calibrations.

Wavenumber selectivity: the maximum absorbance is centered at 690 nm. Comparing the curves in the same conditions, these give similar value on different calibration sets.

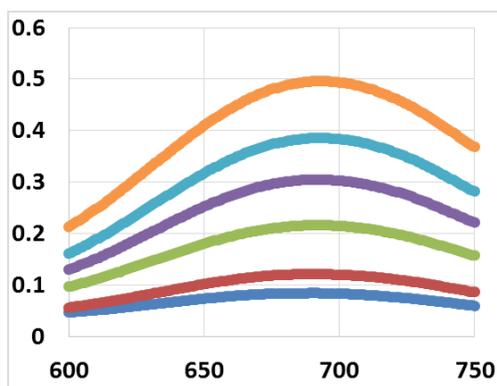


Figure S3b Wave scan of the solution to select the detection wavenumber of the light.

1c. Reaction conditions

All the electrochemical measurements were carried out on AMEL 2551 at 20°C. Pt wire was used as the counter electrode. All the potentials were measured against Ag/AgCl reference electrode (3.0 M KCl). A catalyst deposited membrane electrode with 2 cm^2 active area was used as working electrode that separated the cathode and anode part of the cell. 10 mL/min of N_2 (purity, 99.9999%) was introduced to the cathode part of the system from 30 min before till the end of the reaction.

1d. Calculations

Ammonia formation rates were calculated using the following equation:

$$r_{NH_3} (\mu g \cdot mg_{eCAT}^{-1} \cdot h^{-1}) = \frac{x(ppm) \cdot V(l)}{M_{CAT} (mg) \cdot t(h)}$$

Where:

r_{NH_3} : ammonia formation rate in $\mu g \cdot mg_{eCAT}^{-1} \cdot h^{-1}$.

x (ppm): ammonia concentration in the detection solution in ppm (mg/L)

V (l): is volume of solution in liter.

M_{eCAT} (mg): the amount of the electrocatalyst (mg) in the electrode

t (h): the reaction time in hours.

Turnover frequency (TOF, h^{-1}) is calculated using the following equation:

$$TOF(h^{-1}) = \frac{r_{NH_3} \cdot 159,7}{17 \cdot 10^3 \cdot x_{Fe_2O_3}}$$

Where:

r_{NH_3} : ammonia formation rate in $\mu g \cdot mg_{eCAT}^{-1} \cdot h^{-1}$.

17 and 159,7: the molecular masses of NH_3 and Fe_2O_3 , respectively

$x_{Fe_2O_3}$: the fraction of Fe_2O_3 equivalent present in the electrocatalyst

Faraday efficiency of ammonia was determined using the following equations:

$$FE_{NH_3}(\%) = \frac{3 \times r_{NH_3}^* (mol \cdot cm^{-2} \cdot s^{-1}) \times t(s) \times S(cm^{-2}) \times F}{I(A) \times t(s)} \times 100\%$$

Where:

F: Faraday constant,

I(A): the average of current during the reaction,

$P_{H_2}(\%)$: is the percentage of H_2 in the total gas flow.

$F_{N_2}(mL/min)$: the flow of N_2 , $F_{N_2}(mL/min)=10 mL/min$ in the study.

V_m : the molar volume in the standard condition ($V_m = 22.4 L/mol$).

2. XRD profile of Fresh Fe_2O_3 -CNT and activated catalysts

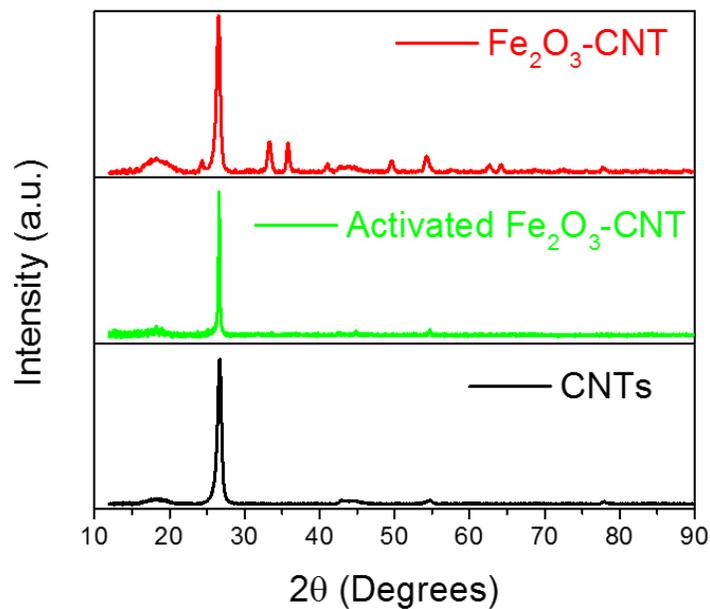


Figure S4a XRD profile of *Fresh* Fe_2O_3 -CNT and of the activated catalysts (the same diffraction patterns from 1h to 24h).

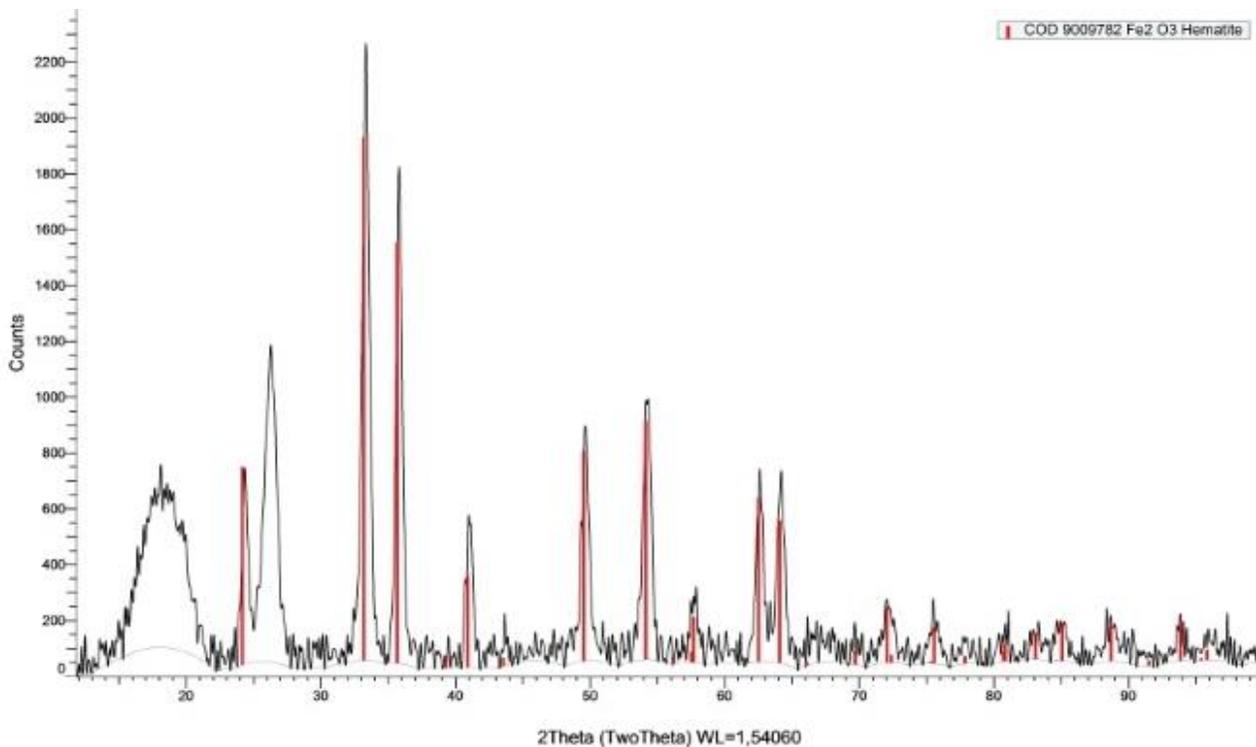


Figure S4b. XRD pattern of *Fresh* Fe_2O_3 -CNT sample.

3. Electron microscopy characterization of the starting electrocatalyst

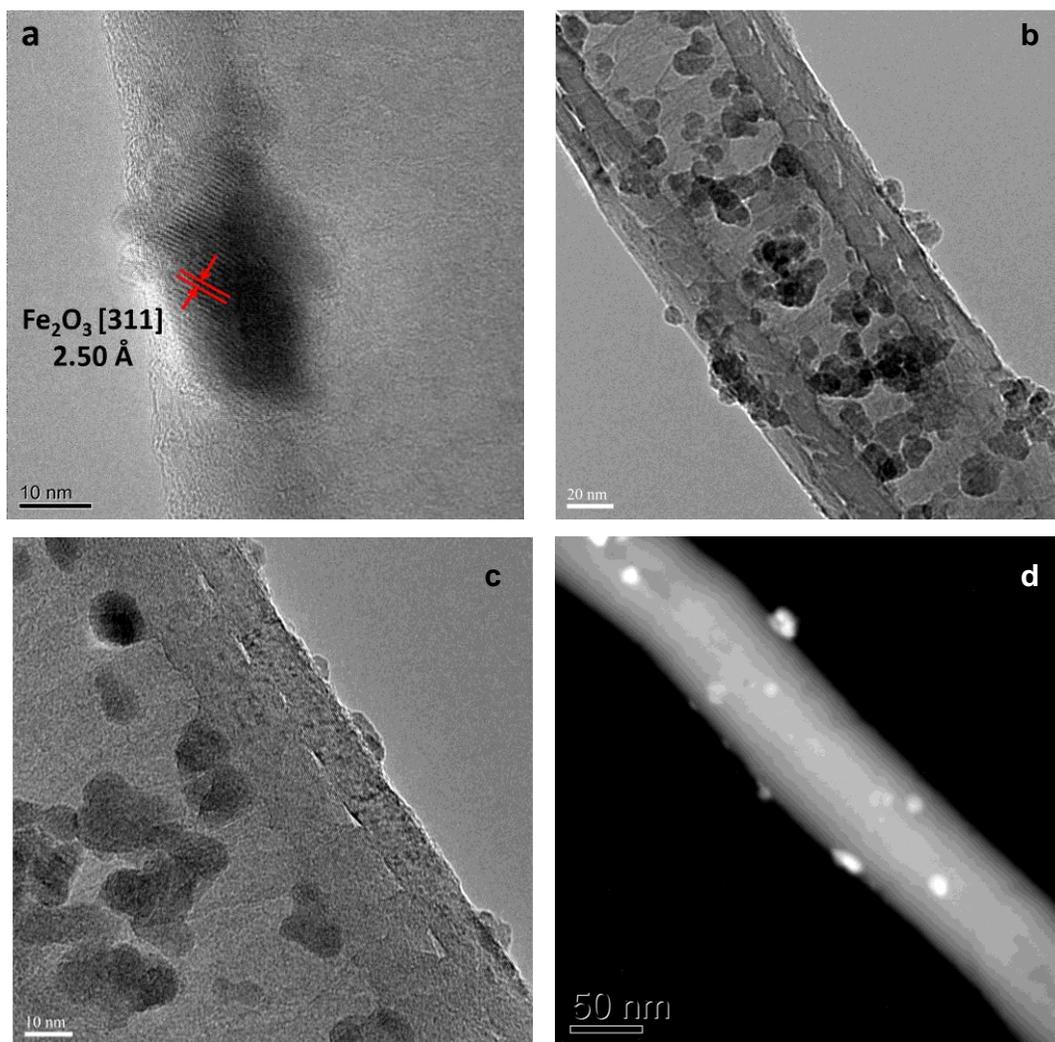


Figure S5a a-c) HRTEM and d) STEM images of *Fresh Fe O₃-CNT*.

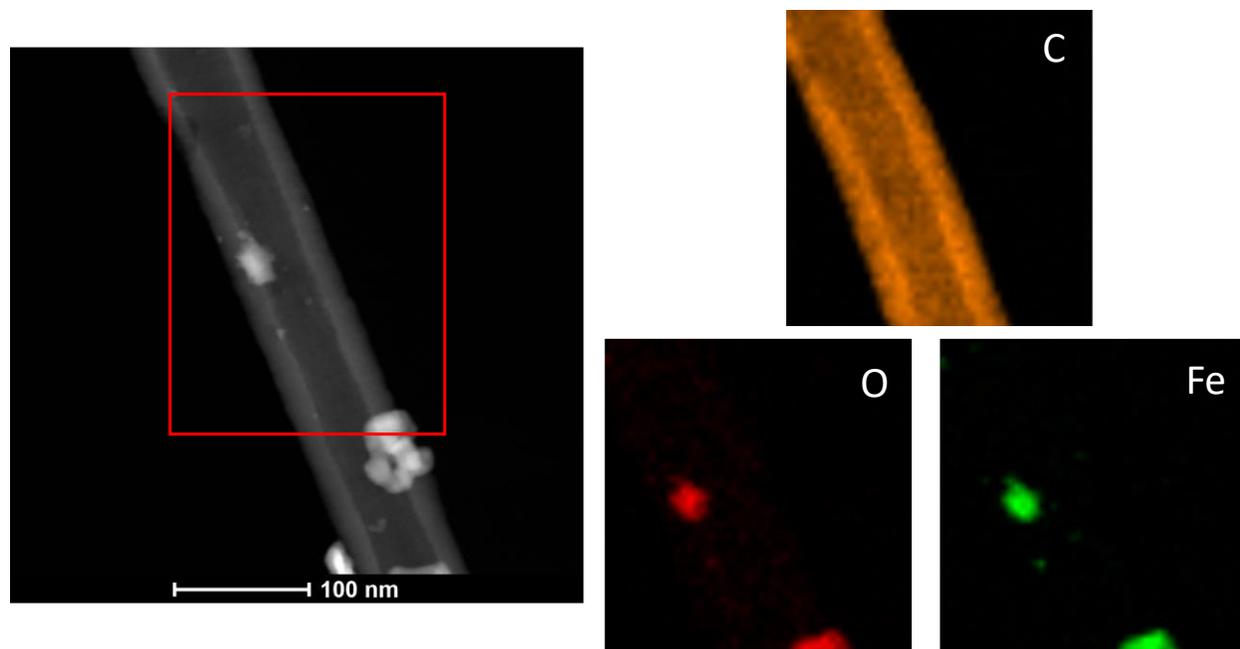


Figure S5b STEM/EDX elemental mapping of *Fresh Fe O₃-CNT*.

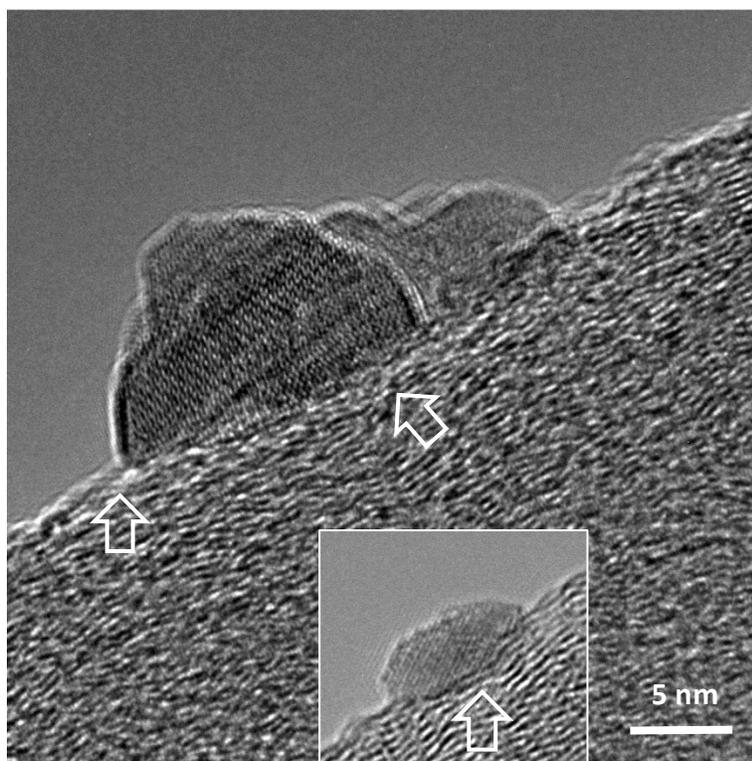


Figure S6 HRTEM image of *Fresh Fe O₃-CNT*; the arrows indicate defect sites in CNTs.

4. HRTEM and STEM of activated electrocatalyst

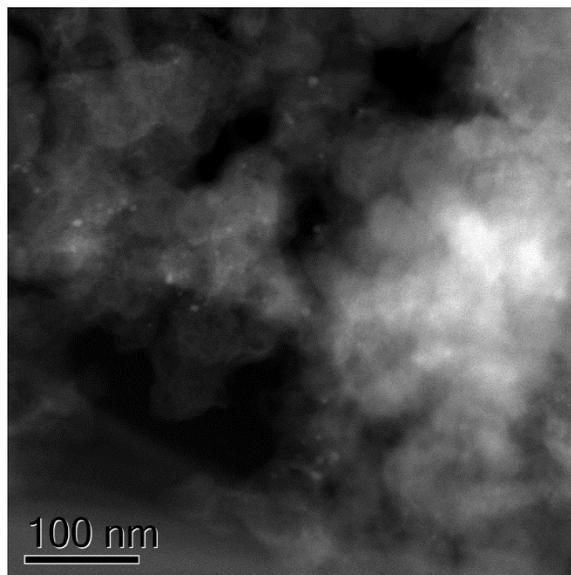


Figure S7a STEM of iron oxide particles mixed with amorphous carbon (from carbon paper)



Figure S7b STEM and HRTEM of activated 1h, which shows the reconstruction process of iron oxide particle

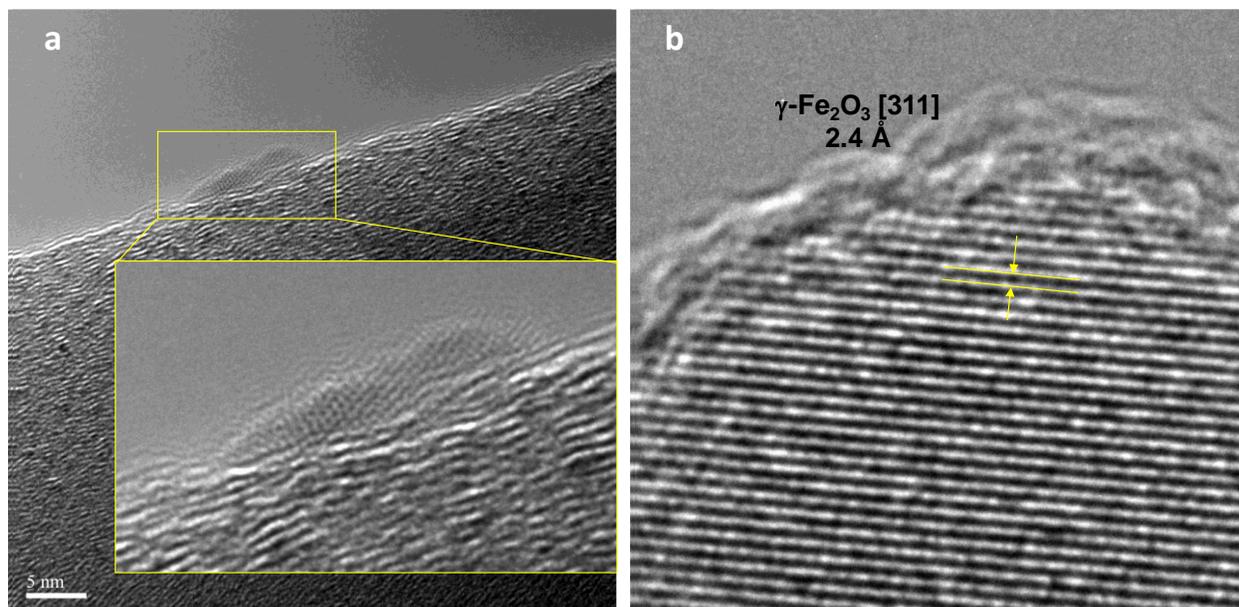


Figure S7c HRTEM of activated 1h nanoparticles. Regular fringes are observed in the nanoparticle with a spacing of 0.24 nm, which is the (311) interplanar distance of the cubic maghemite.

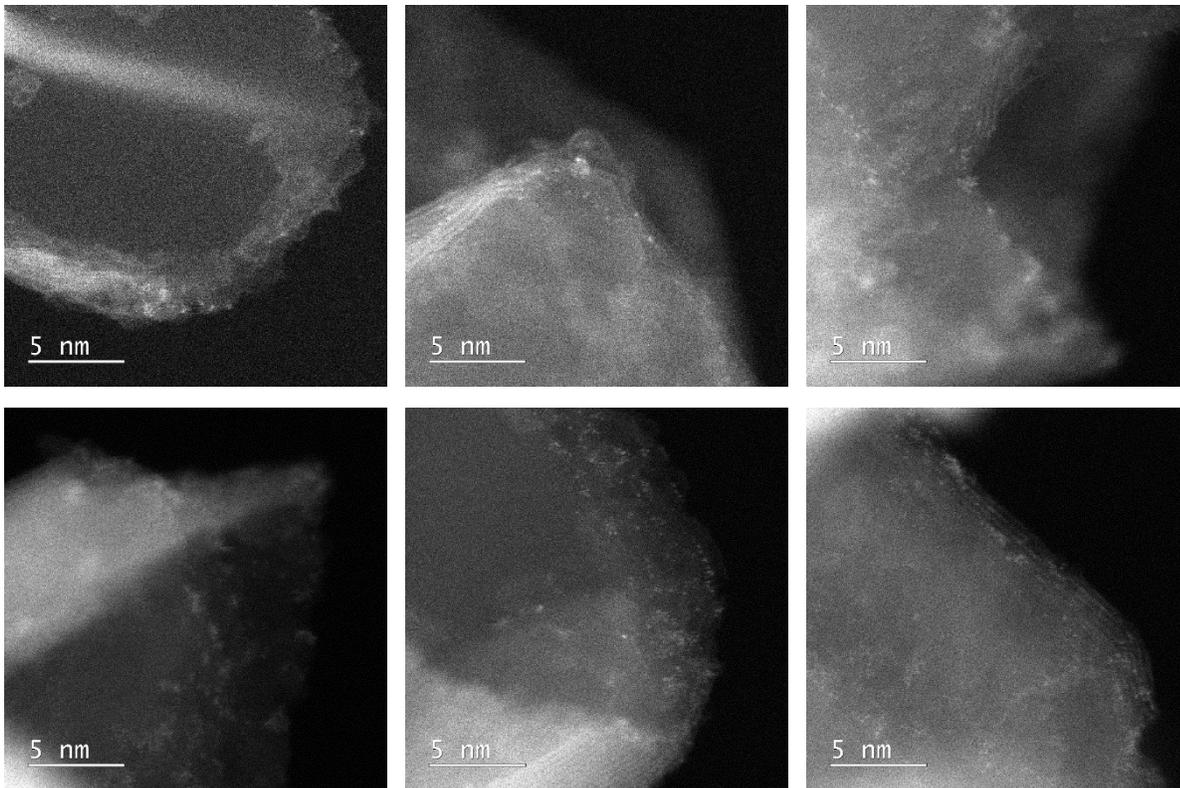


Figure S7d STEM and HRTEM of activated 3 h,

5 XPS experiments

5a. Deconvolution information of O1s

| Time (h) | Total O1s (%) | O1 (Fe-O-Fe) (%) | O2 (Fe-O-H) (%) | O3 (C-O-C) (%) | O4 (C-O-H) (%) |
|----------|---------------|------------------|-----------------|----------------|----------------|
| Fresh | 9.01 | 4.03 | 0.35 | 2.40 | 2.09 |
| 1 h | 5.12 | 1.96 | 0.80 | 1.31 | 1.05 |
| 3 h | 5.53 | 2.23 | 0.54 | 1.29 | 1.49 |
| 6 h | 4.52 | 1.47 | 0.35 | 1.31 | 1.38 |
| 24 h | 3.33 | 1.23 | 0.61 | 1 | 0.49 |

Table S1. Deconvolution data for XPS O1s spectra in Fresh Fe₂O₃-CNT and activated samples at different times.

5b. XPS test of electrocatalysts after reaction (Fe2p)

Figure S8 shows that in all the electrocatalysts after testing tested only traces of Fe⁰ are detected. This indicates that under the current experimental conditions used (applied voltage of -1.0V vs. RHE) the iron oxide species were not reduced to metallic iron.

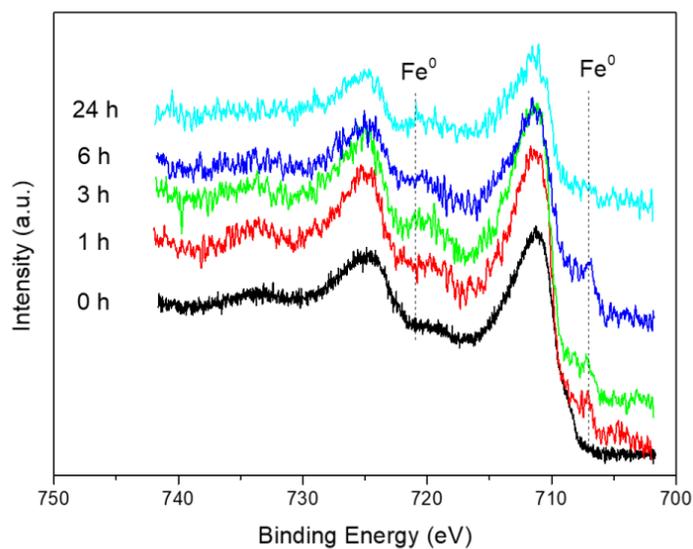


Figure S8. Fe 2p XPS spectra of *Fresh Fe₂O₃-CNT* and activated samples at different times.

5c. XPS profile

N1s spectra for pristine CNT and o-CNT

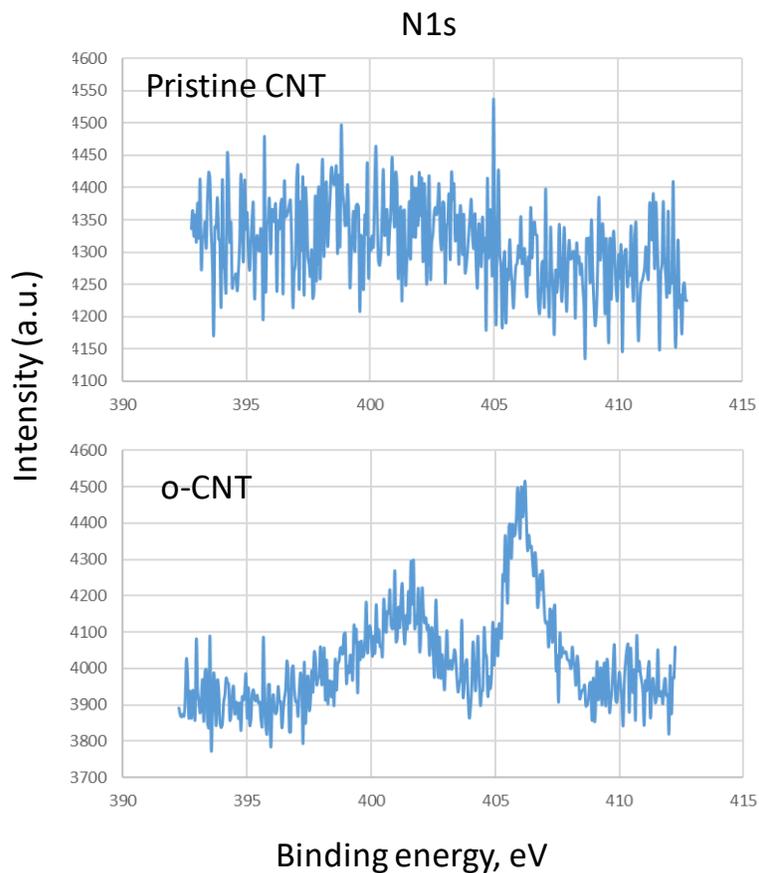


Figure S9a. N1s XPS spectra for pristine CNT and after oxidative activation with HNO₃ (o-CNT).

A very weak N1s signal is present in o-CNT, but not in pristine CNT, due to some residual nitric acid after the oxidative treatment.

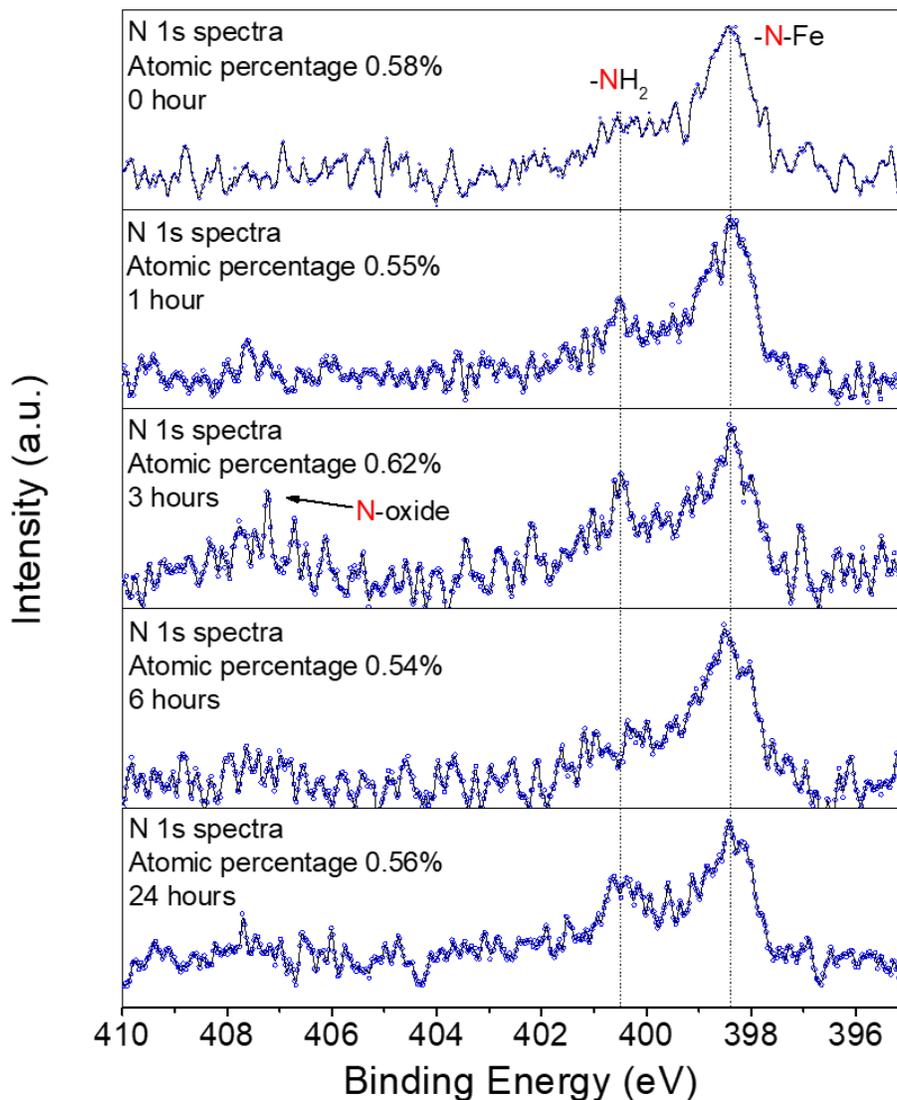


Figure S9b. N1s XPS spectra of Fe₂O₃-CNT samples after different times of operations at a constant voltage of -1.0 V vs. RHE.

A weak signal of N was detected in the fresh catalysts (0 hour), deriving from the oxidative pretreatment of CNT and the possible incomplete removal of nitrate from the Fe(NO₃)₃ used as precursor for the preparation of electrocatalysts. The intensity of the signal of N does not change during the activation pretreatment, indicating that it is not involved in the formation of ammonia. Additionally, N species in N-O structure was observed after the 3h of reaction. This might be due to the interaction of N₂ with O₂ during ex-situ XPS experiments.

Fe₂O₃ before and after annealing with Ar

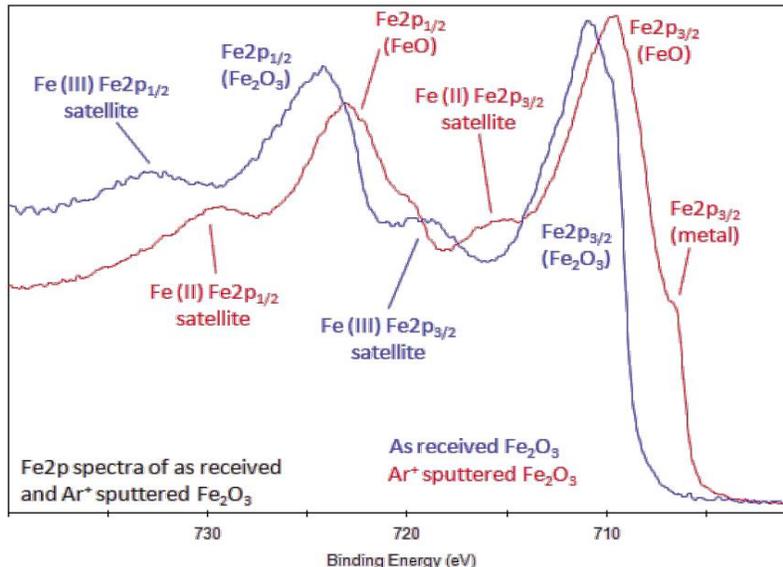


Figure S9c. Fe 2p XPS profile of Fe₂O₃ before and after sputtering with Ar (adapted from Thermo XPS website - <http://xpssimplified.com/elements/iron.php>).

Peak position and FWHM of the XPS Fe2p peak for Fe2p_{3/2} and Fe2p_{1/2}

| Sample | Fe2p _{3/2} B.E. (eV) | Fe2p _{3/2} FWHM (eV) | Fe2p _{1/2} B.E. (eV) | Fe2p _{1/2} FWHM (eV) |
|-----------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| maghemite | 710.9 | 3.5 | 724.5 | 3.9 |
| magnetite | 710.4 | 4 | 723.9 | 4.1 |
| hematite | 710.9 | 3.6 | 723.8 | 4.2 |

Table S2. Peak position and FWHM of the XPS Fe2p peak for Fe2p_{3/2} and Fe2p_{1/2}. Reproduced as reference from T. Radu, C. Iacovita, D. Benea, R. Turcu, Applied Surface Science 405 (2017) 337-343.

6 Onset potential of Fe₂O₃-CNT/C

Liner sweep voltammetry (LSV) test was performed under the following conditions: 0.5M KHCO₃ as electrolyte, 10mL/min N₂ and scan speed was 1 mV/s from -200 mV to -2500 mV. Accord to the profile, the onset potential of Fe₂O₃-CNT for N₂ reduction is lower than -1.5V vs. Ag/AgCl in our cell

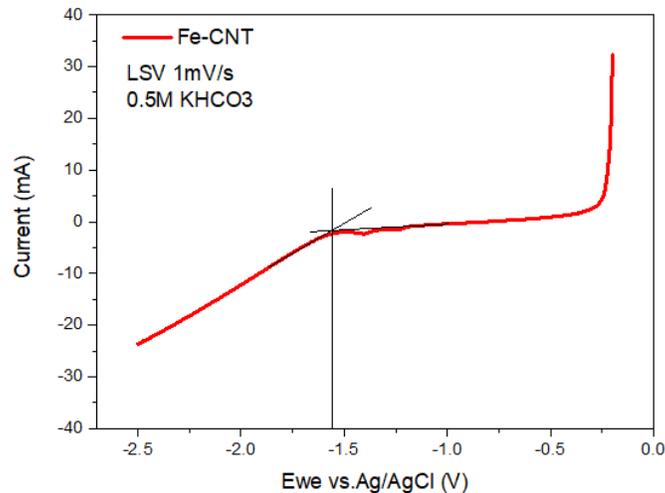


Figure S10. Onset potential of Fe₂O₃-CNT in this cell.

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