Supporting information

Cations Distribution: A Descriptor for Hydrogen Evolution Electrocatalysis on Transition-Metal Spinels

Aya K. Gomaa[a], Maram G. Zonkol[a], Ghada E. Khedr[,b], Nageh K. Allam[a]*

[a]Energy Materials Laboratory, Physics Department, School of Sciences & Engineering, The American University in Cairo, New Cairo 11835, Egypt

[b]Department of Analysis and Evaluation, Egyptian Petroleum Research Institute, Cairo 11727, Egypt

*Corresponding Author's email: nageh.allam@aucegypt.edu

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Faradaic efficiency (FE) calculations:

To measure the faradaic efficiency of the hydrogen produced from $CoFe_2O_4$/Ni foam, water displacement method was applied. Chronopotentiometry was performed at a current density of 20 mA/cm^2 for 1h. The amount of hydrogen and oxygen produced was collected and measured via an inverted 10ml measuring cylinder in a sink of water.

Following the amount of hydrogen produced was calculated theoretically and experimentally to calculate the FE using the following equations.

Amount of hydrogen theoretically:

- The number of electrons used to produce hydrogen = Q applied at certain time/ Faraday's constant.
- Every one mole of H_2 produced $2e^-$ are required.
- No. of moles of hydrogen produced (n) = No. of electrons /2.

Amount of hydrogen experimentally:

- No of moles of hydrogen produced = amount of the displaced volume of water (L) / 22.4

$$\% \ FE = \frac{No.\ of\ moles\ of\ Hydrogen\ produced\ experimentaly}{No.\ of\ moles\ of\ Hydrogen\ produced\ theoretically} * 100$$

Turnover frequency (TOF) calculations:

TOF of the electrocatalyst is a critical kinetic parameter that indicates the speed at which an electrocatalyst can catalyze a specific electrochemical reaction. TOFs for both HER and OER mechanisms can be calculated per unit time using the following formula, based on the pseudo-first-order kinetics, as reported in previous studies.

$$TOF = \frac{jN_A}{nF\Gamma}$$

where j is the current density (mA/cm^2) measured, N_A is the Avogadro number, F is Faraday constant (96485), n is the number of electrons transferred (which is for HER=2, and OER= 4), and Γ is the moles of the surface-active sites included within the used catalyst.

Therefore, the total number of H_2 produced per geometric area was calculated from the current density value extracted from the HER-LSV polarization curve as the following:

$$\# \; H_2 = |J|(mA/cm^2) * (\frac{1 \; C/s}{1000 \; mA}) * (\frac{1 \; mol \; e^-}{96485}) * (\frac{1 \; mol \; H_2}{2e^-}) * (\frac{6.023x10^{23} H_{2 \; molecules}}{1 \; mol \; H_2})$$

$$= 3.12 \; x \; 10^{15} \; \frac{H_{2 \; S}-1}{cm^2} \; per \; \frac{mA}{cm^2}$$

Since the total number of active sites are not precisely determined the exact number of binding sites for H_2 are not determined exactly. We calculated the total number of active sites as the total number of the surface sites from the unit cell of the catalyst ($CoFe_2O_4$) which could possibly underestimate the real TOF values.

From the crystal structure of $CoFe_2O_4$, we can calculate the number of active sites according to following equations:

$$\# \; Surface \; sites = (\frac{56 \; atoms \; per \; unit \; cell}{602.58 \; Å^3 \; per \; unit \; cell})^{\frac{3}{2}}$$

$$TOF_{HER} = \frac{3.15 * 10^{15} * |J|}{\# \; Surface \; active \; sites * A \; (ECSA)} = \frac{3.15 * 10^{15} * |J|}{2.05 * 10^{15} * 241.5}$$
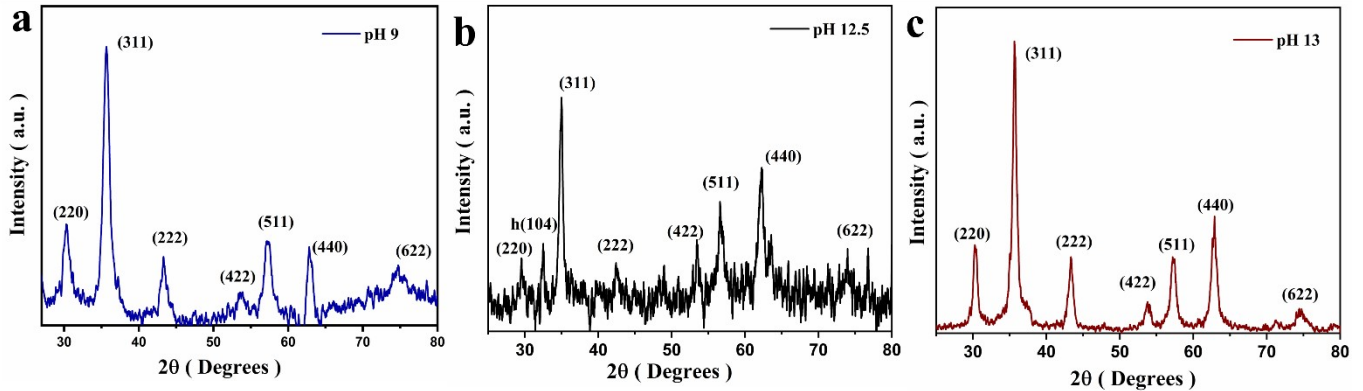
Figure S1. XRD spectrum of CoFe$_2$O$_4$ powder prepared at pH (a) 9, (b) 12.5 and (c) 13. The peak at 32.5⁰ in (b) is assigned to hematite (104).
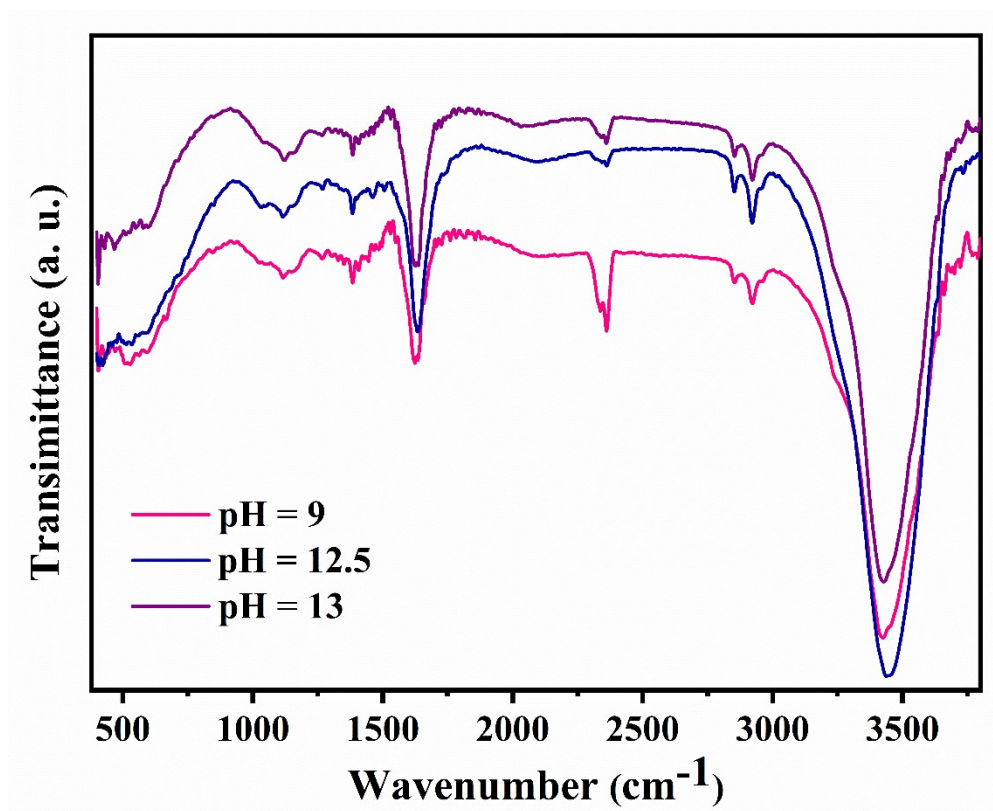

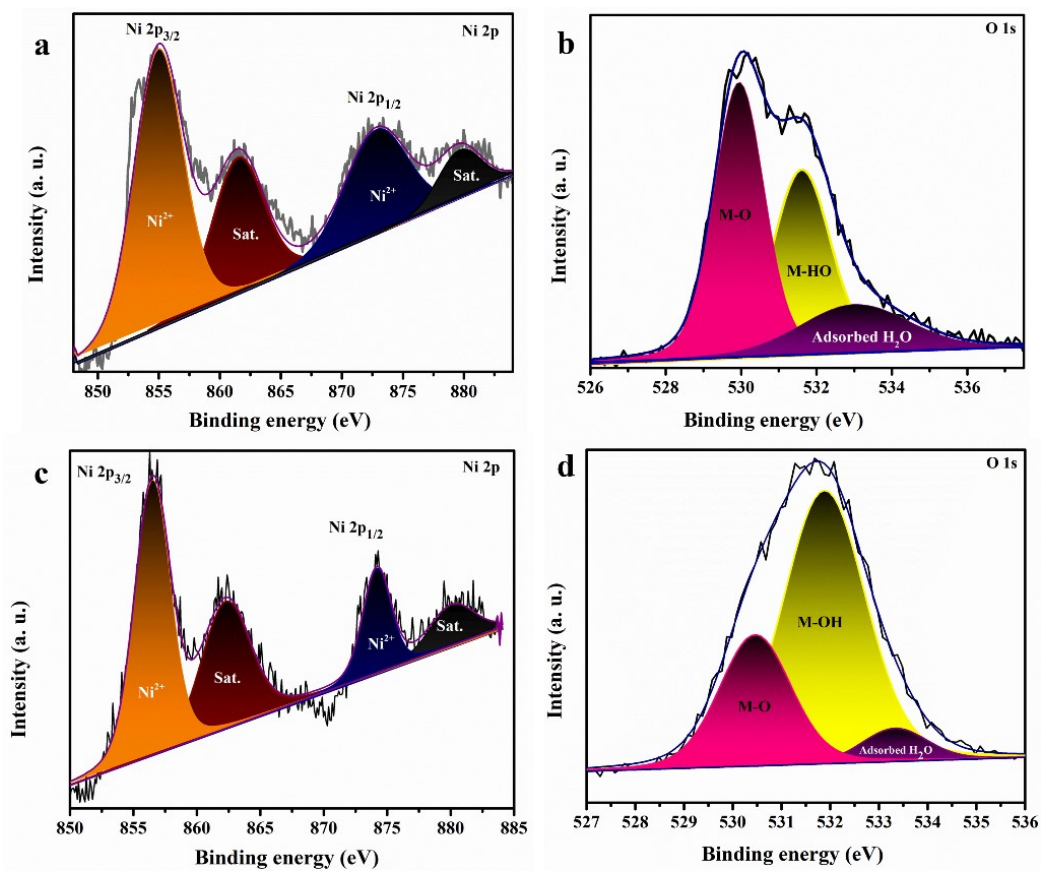**Figure S2.** Full FTIR spectrum of CoFe$_2$O$_4$ powder prepared at pH (a) 9, (b) 12.5, and (c) 13.

Figure S3. XPS spectrum of CoFe$_2$O$_4$/Ni foam. (a) Ni 2p. (b) O 1s for pH 9 sample and (c) Ni 2p, and (d) O 1s for pH 13 sample.
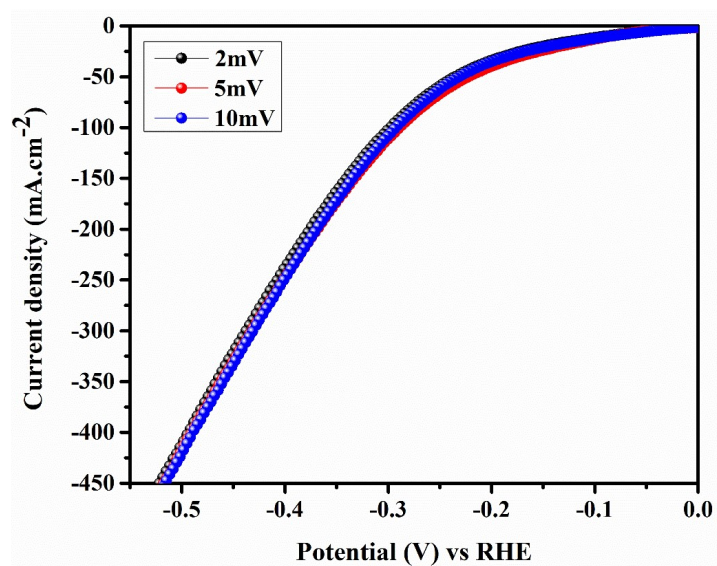

Figure S4. iR-corrected LSV at different scan rates (2, 5, 10 mV/s) for pH 9 sample
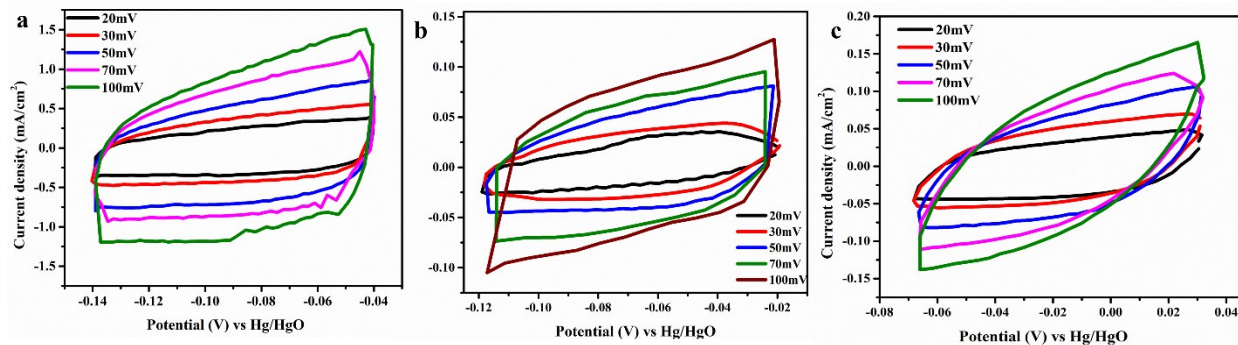
Figure S5. Determination of ECSA for CoFe$_2$O$_4$/Ni foam prepared at different pHs. CV scans at different scan rates (20 -100 mV s^{-1}) in 1 M KOH for the catalysts prepared at a) pH 9, b) pH 12.5, and c) pH 13.
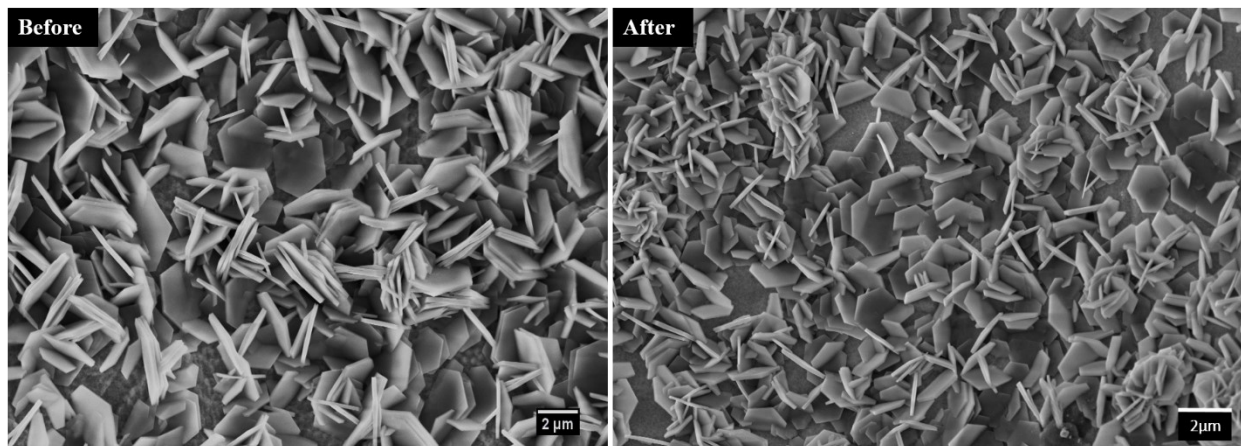

Figure S6. SEM of CoFe$_2$O$_4$/ Ni foam catalyst prepared at pH 9 before and after CP stability test for 44 h of continuous electrolysis.

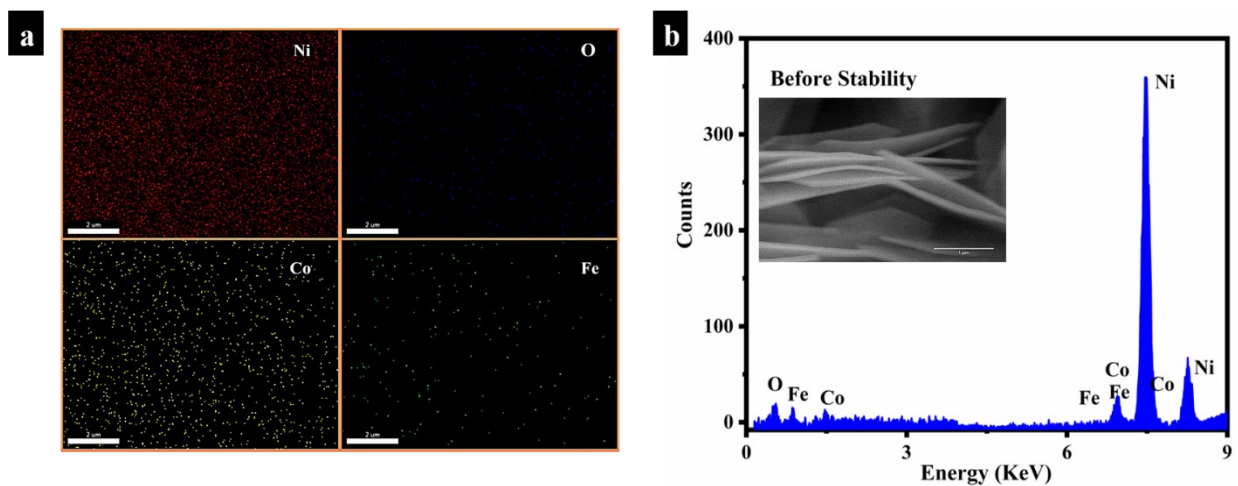**Figure S7.** EDS of CoFe$_2$O$_4$/ Ni foam catalyst prepared at pH 9 before CP stability test for continuous electrolysis.

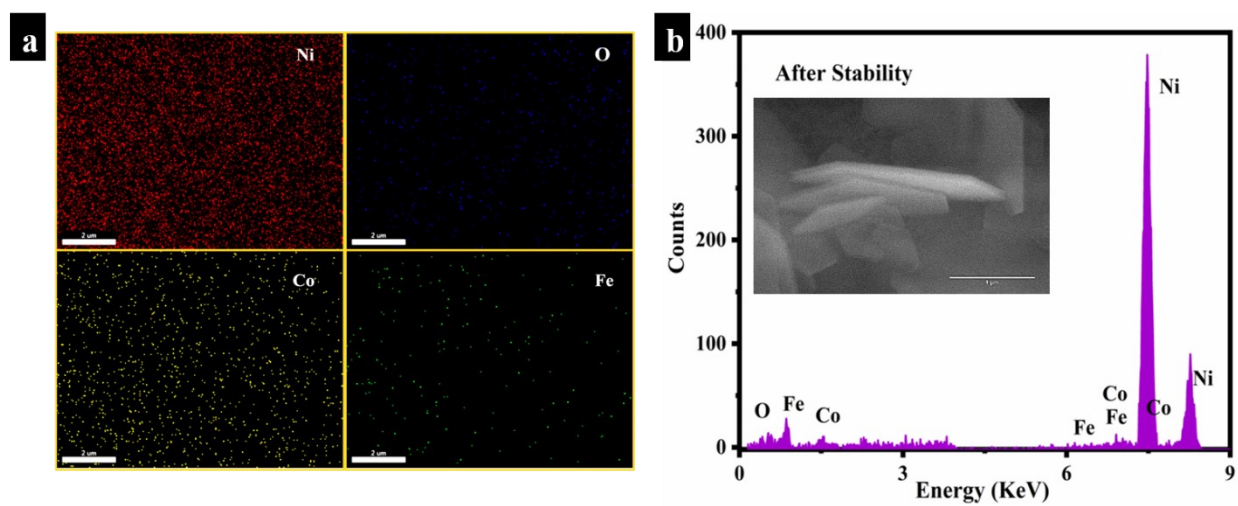**Figure S8.** EDS of CoFe$_2$O$_4$/ Ni foam catalyst prepared at pH 9 after CP stability test for continuous electrolysis.

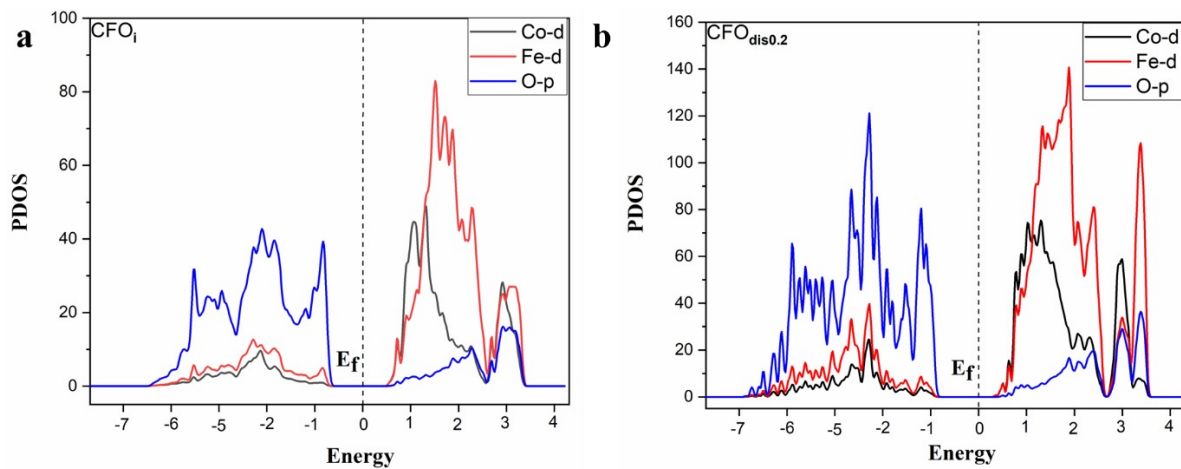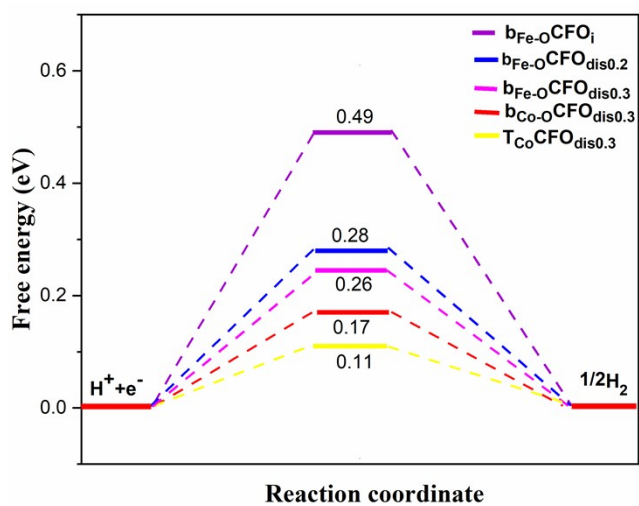**Figure S9.** PDOS for a) CFO$_i$ and b) CFO$_{dis0.2}$

Figure S10. HER free energy diagram for catalysts without Ni foam.

Table S1. The electrocatalytic activity of our catalyst compared to those recently reported in the literature.

Catalyst	Overpotential (mV) @ -10mA/cm^2	Tafel slope (mV dec^{-1})	Ref.
CoFe$_2$O$_4$/Ni Foam (δ=0.33)	66	67	This Work
CoNi/CoFe$_2$O$_4$/Ni foam	82	96	1
Co$_3$O$_4$-800/GC	93	122.1	2
NiFe-oFe$_2$O$_4$@Co$_3$S$_4$/CFP	98	78.2	3
Ti$_3$C$_2$–CoFe$_2$O$_4$/g-C$_3$N$_4$	223	48.5	4
CoNiFe$_2$O$_4$ + Se$_x$	173.5	91	5
CoFe$_2$O$_4$ - graphene	248.3	116.6	6
NiFe$_2$O$_4$ - graphene	259	121.4	6
FeSe$_2$/CoFe$_2$O$_4$	231	88.76	7
CoFe$_2$O$_4$ ED@NF	270	94	8
CoFe$_2$O$_4$/ SWNTs	263	46	9
Ag@CoFe$_2$O$_4$/g-C$_3$N$_4$	259	76.1	10

Table S2. The current densities normalized to ESCA at different potential values for pH 9, 12.5, 13, respectively.

Voltage Vs RHE	pH 9 (Current density in mA cm^{-2}ECSA)	pH 12.5 (Current density in mA cm^{-2}ECSA)	pH 13 (Current density in mA cm^{-2}ECSA)
-0.08	0.055	0.05	0.0013
-0.09	0.6	0.054	0.0015
-0.1	0.068	0.061	0.0016
-0.11	0.077	0.067	0.0017
-0.12	0.087	0.078	0.0021

References

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