Supporting Information

FeNC Catalysts for CO2 Electroreduction to CO: Effect of Nanostructured Carbon Supports

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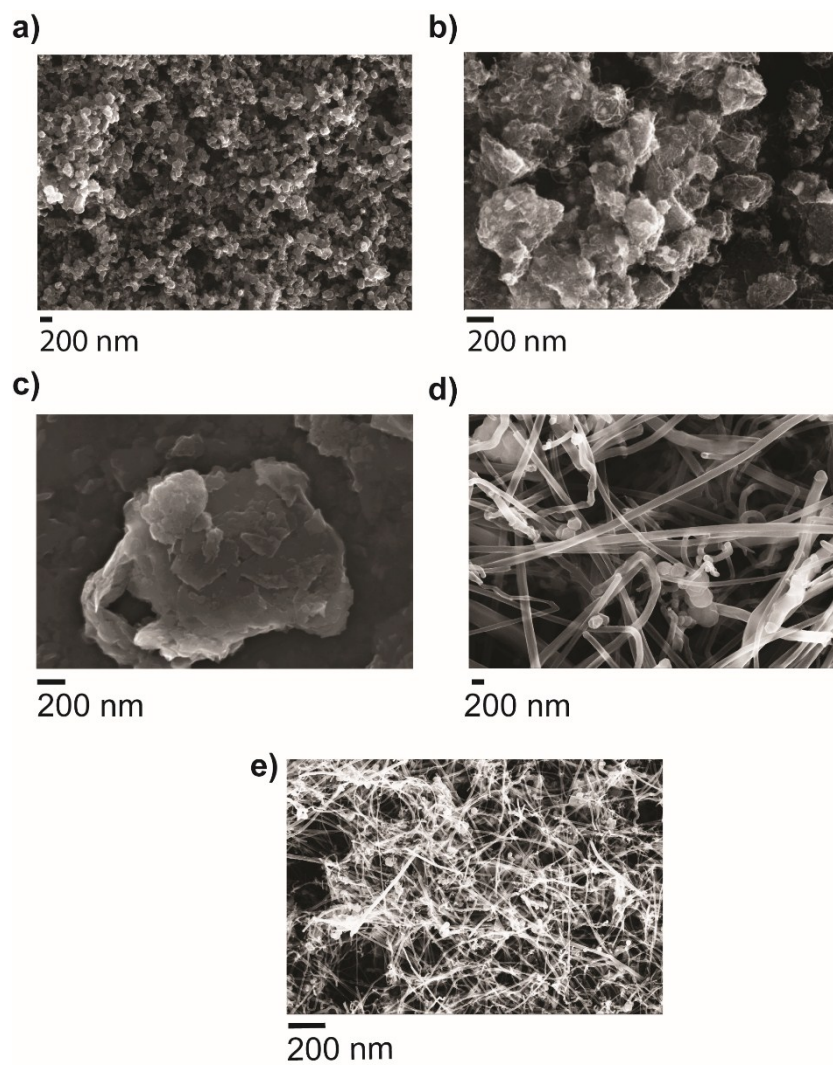KEYWORDS. CO_2 reduction – electrocatalysis – iron - Fe-N-C materials-carbon supports.

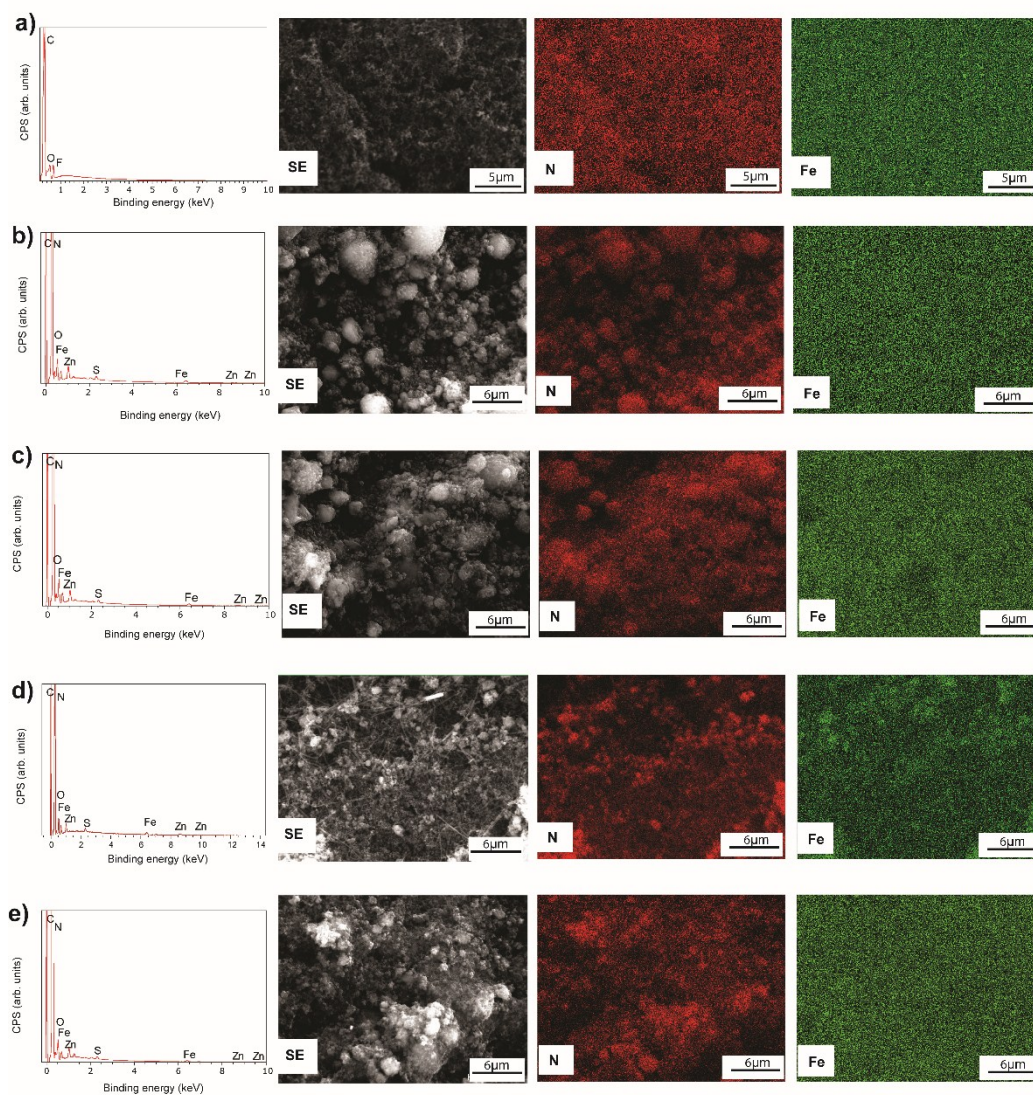**Figure S1.** SEM images of **(a)** bare GDL and **(b)** FeNC, **(c)** rGO**, (d)** CNF and **(e)** CNT deposited on GDL

Figure S2. SEM-EDS analysis of **(a)** bare GDL and **(b)** FeNC **(c)** FeNC-rGO **(d)** FeNC-CNF **(e)** FeNC-CNT. Fe in green and N in red.
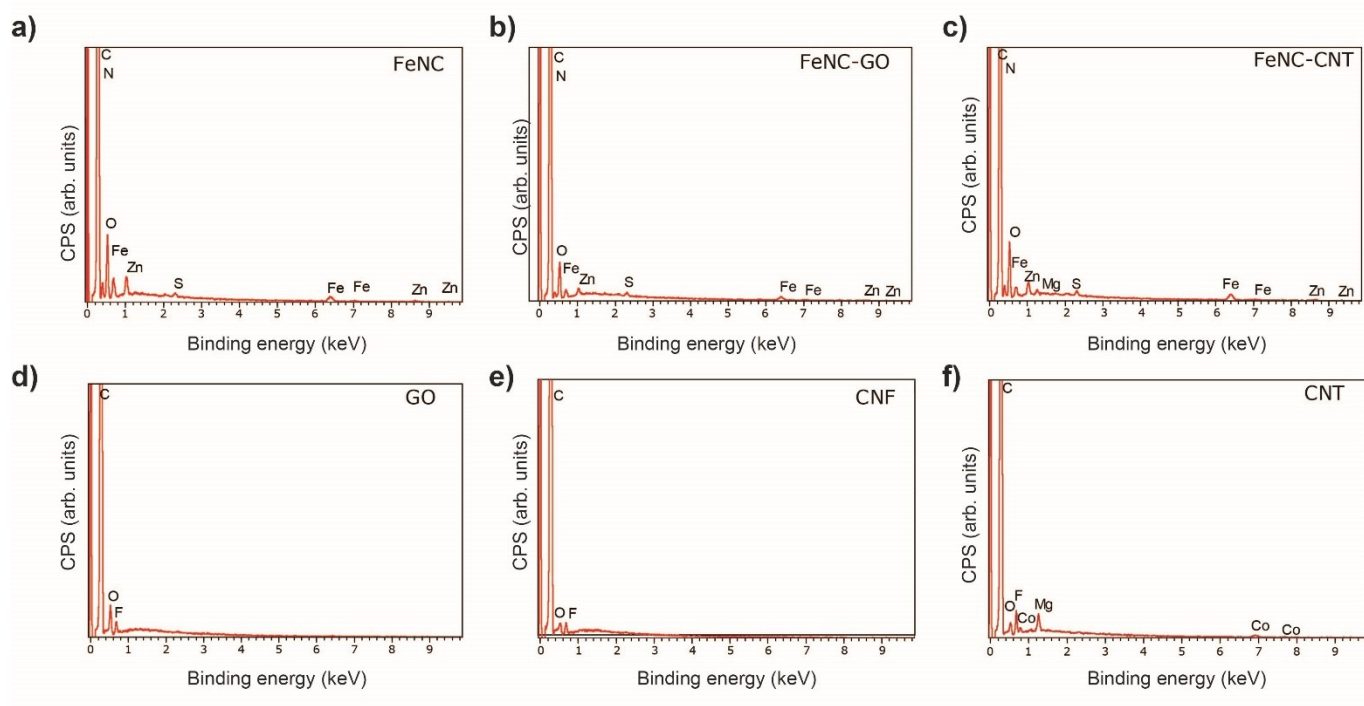
Figure S3. EDS analysis of **(a)** FeNC , **(b)** FeNC-GO, **(c)** FeNC-CNT, **(d)** GO, **(e)** CNF and **(f)** CNT.
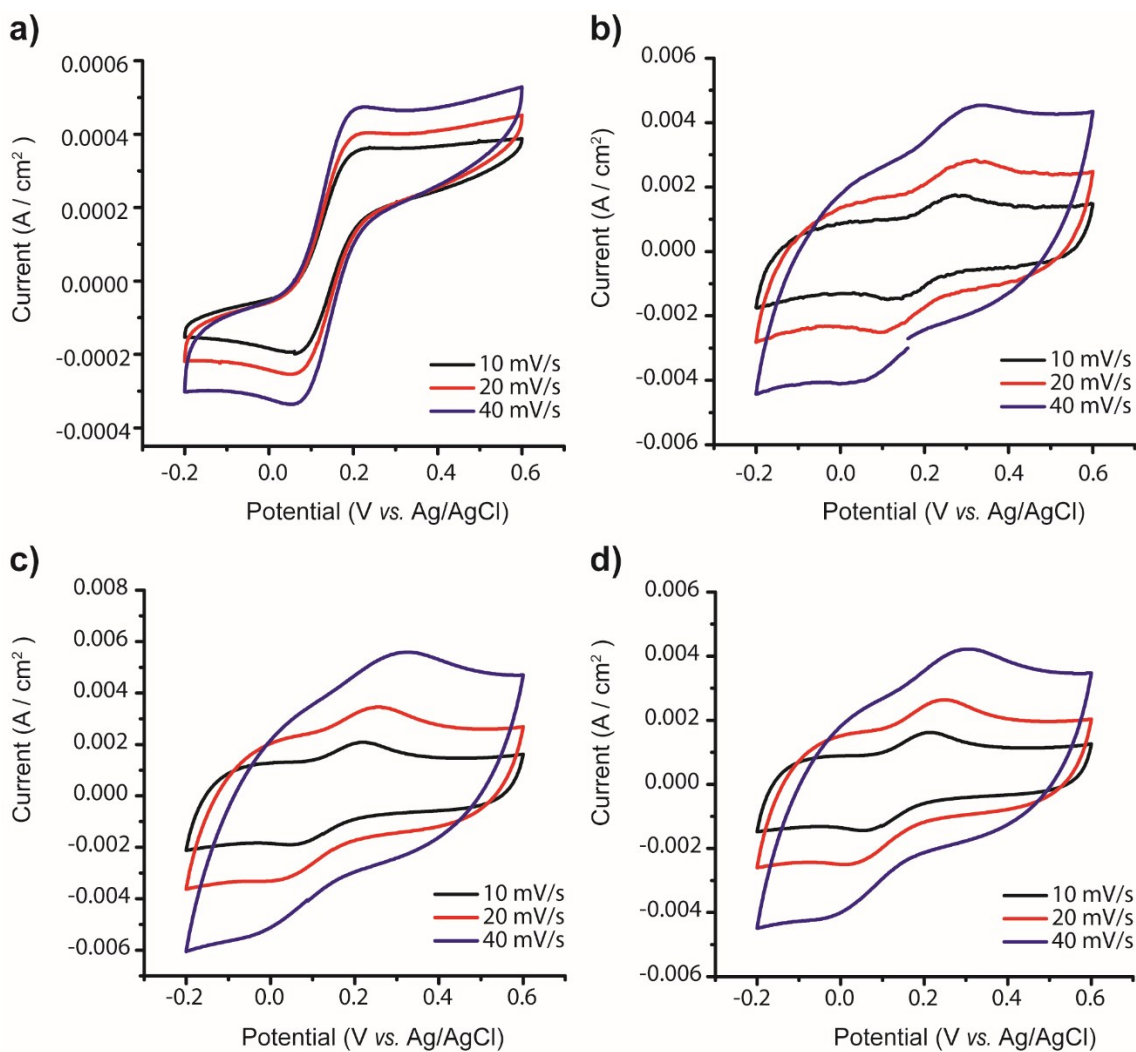
Figure S4. Cyclic voltammograms (CV) of **(a)** FeNC, **(b)** FeNC-rGO, **(c)** FeNC-CNF and **(d)** FeNC-CNT electrodes under conditions of 10 mM ferrocyanide in 0.1 M KCl at various scan rates. Cathodic and anodic peak currents correspond to the redox activity of ferrocyanide.
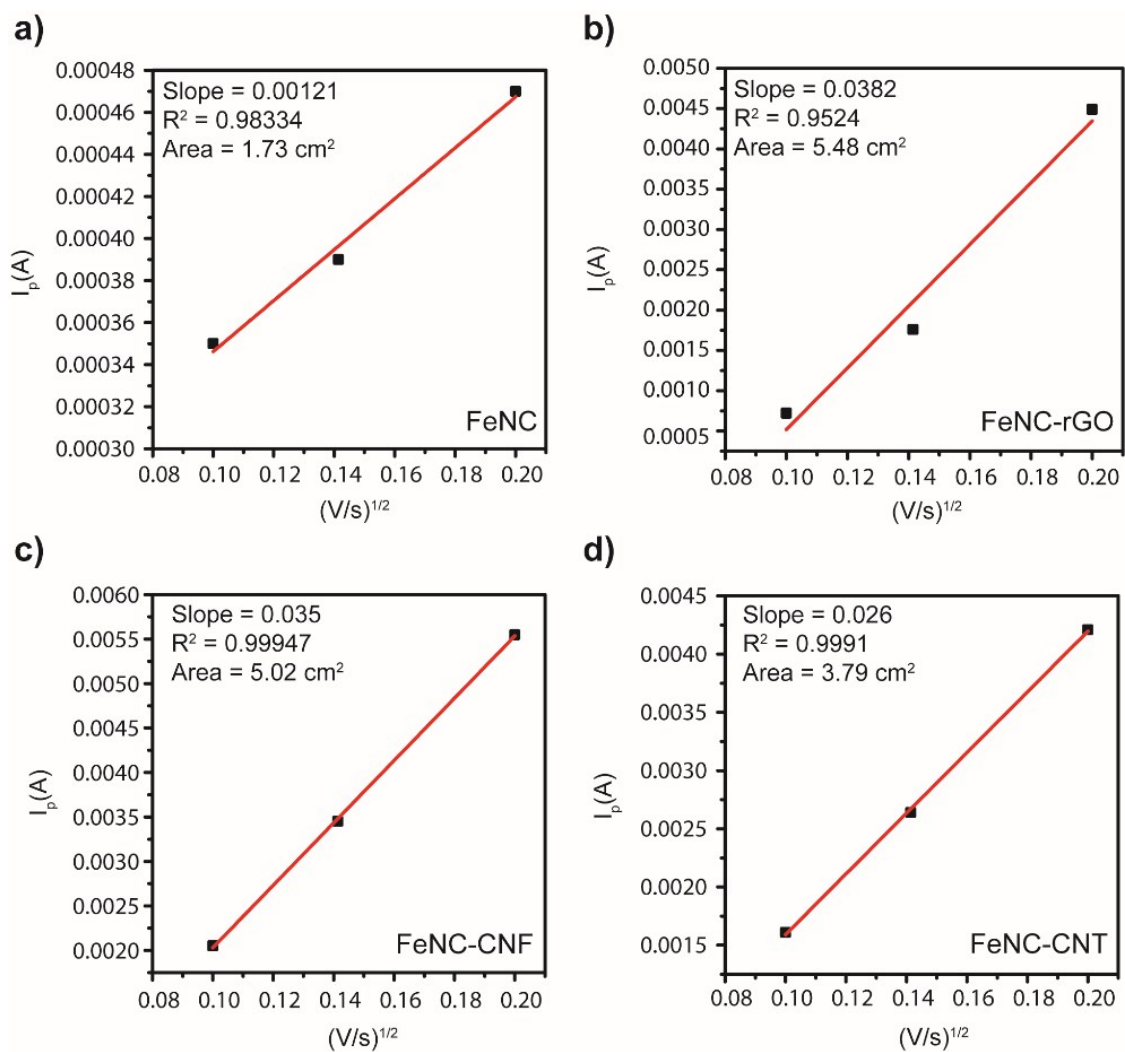
Figure S5. Peak current as a function of the square root of scan rate. Data are derived from the CVs shown in Figure S4, for **(a)** FeNC, **(b)** FeNC-rGO, **(c)** FeNC-CNF and **(d)** FeNC-CNT. The ECSAs are estimated from the slope of the plots.
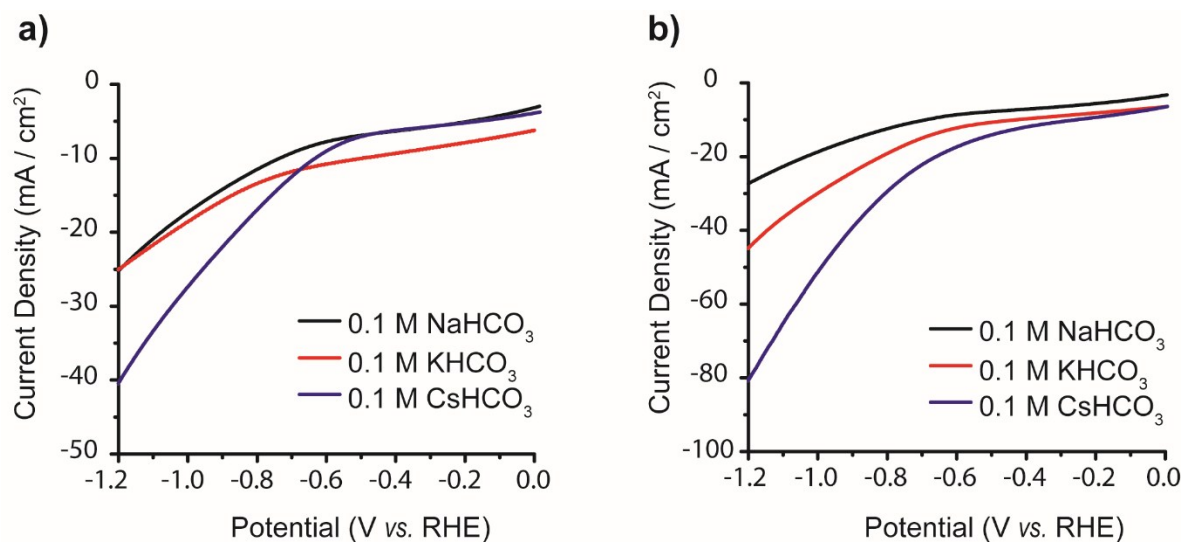
Figure S6. LSVs of **(a)** FeNC-CNF and **(b)** FeNC-CNT electrodes in CO_2-saturated aqueous solutions of various alkali bicarbonates. Scan rate: 10 mV/s.
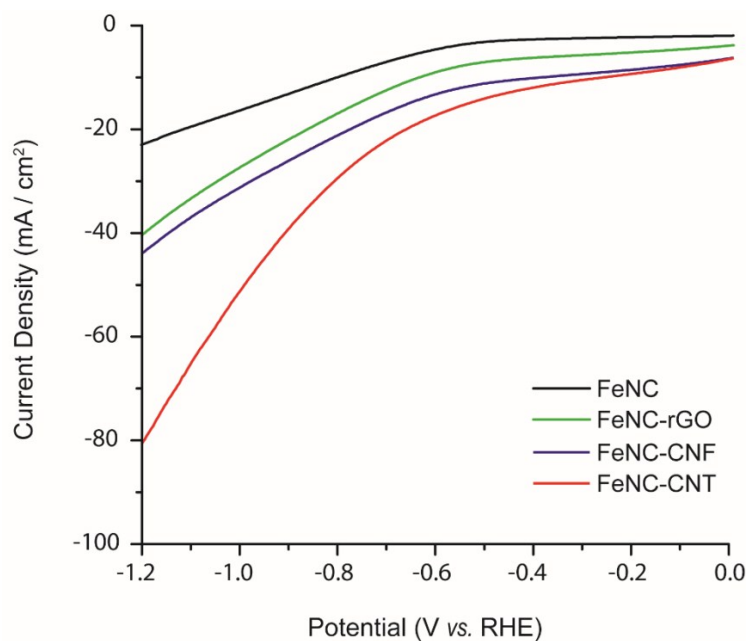

Figure S7. LSVs of FeNC (black), FeNC-rGO (green), FeNC-CNF (blue), and FeNC-CNT (red) electrodes in CO_2-saturated 0.1M $CsHCO_3$ aqueous solutions. Scan rate: 10 mV/s.
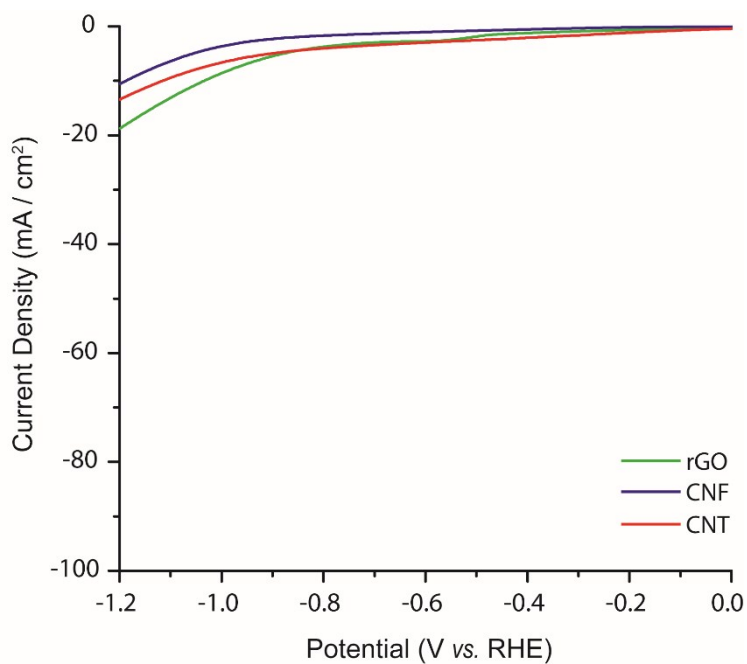
Figure S8. LSVs of rGO (green), CNF (blue) and CNT (red) electrodes in CO_2-saturated 0.1M $CsHCO_3$ aqueous solutions. Scan rate: 10 mV/s.
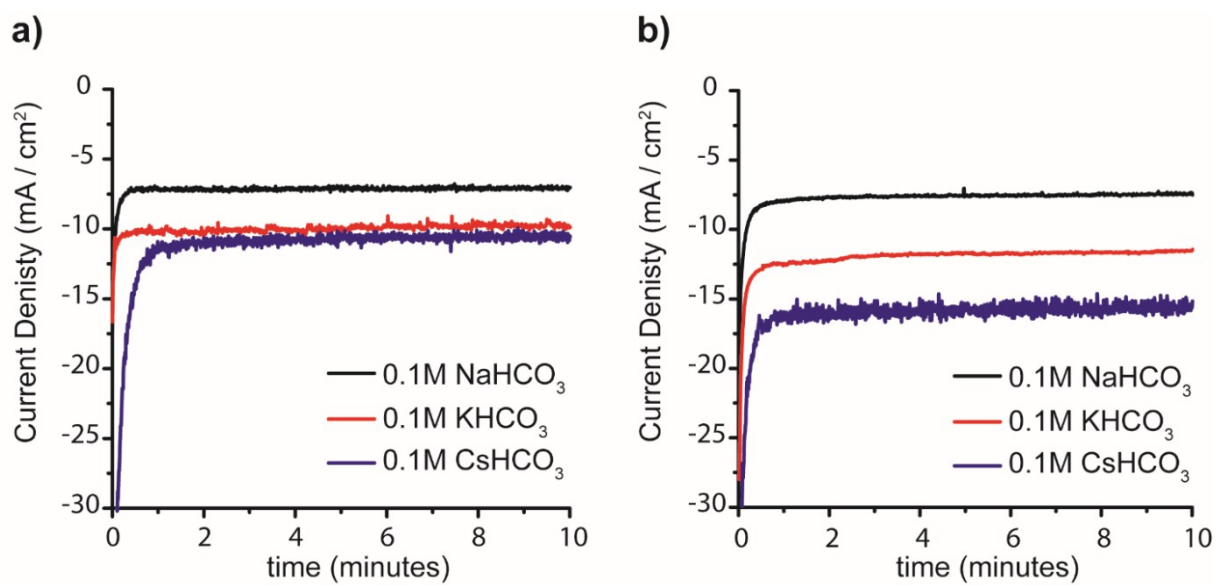

Figure S9. Current density variations during CPE at -0.7 V *vs.* RHE using **(a)** FeNC-CNF and **(b)** FeNC-CNT electrodes in aqueous solutions of various alkali bicarbonates. CO_2 flow: 10 mL/min
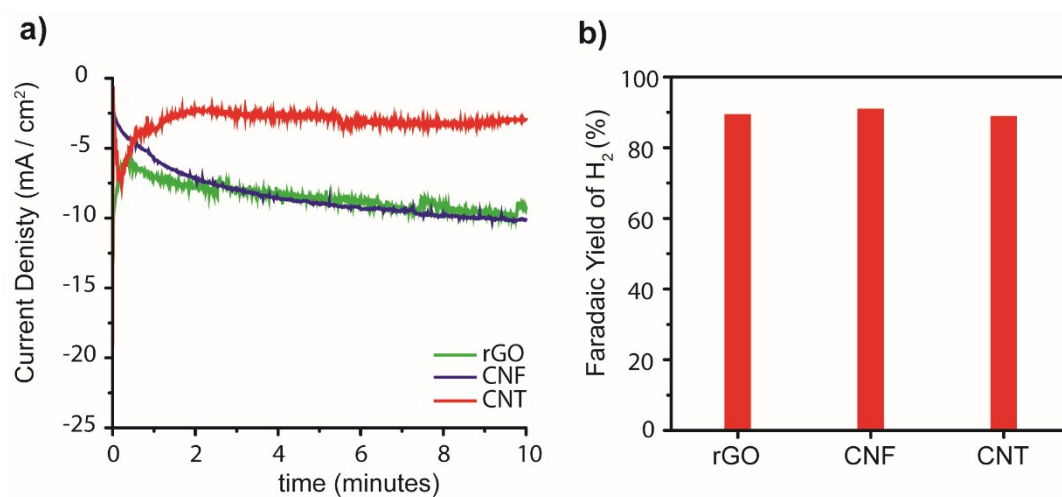
Figure S10. (a) Current density variation during CPE at -0.7 V *vs*. RHE using rGO (green), CNF (blue), and CNT (red) electrodes and **(b)** Faradaic Yields for H_2. CPE conditions: 10 mL/min flow of CO_2 in a 0.1 M $CsHCO_3$ aqueous solution.
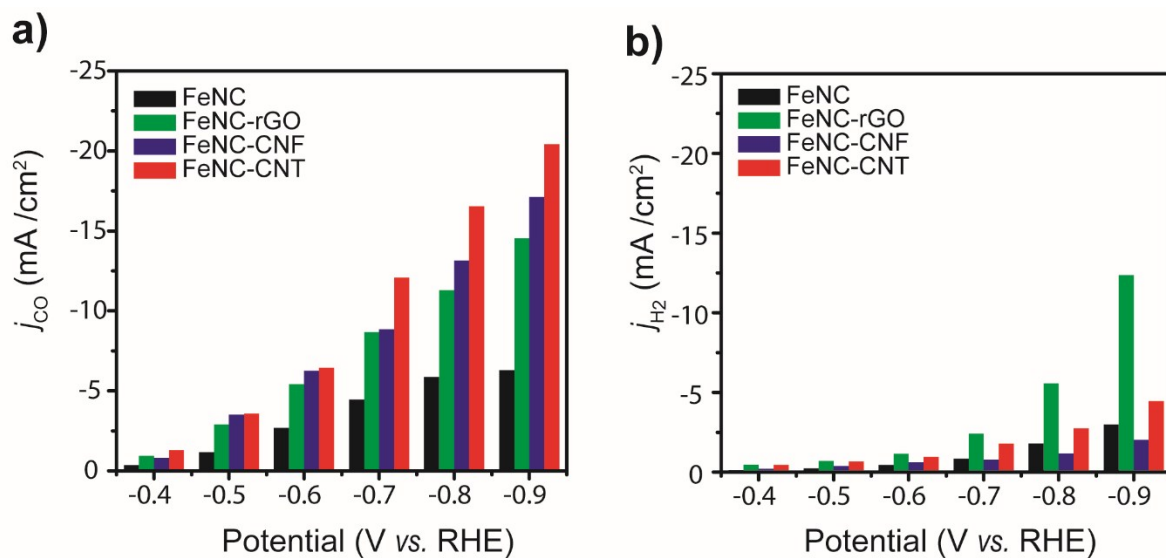
Figure S11. Partial current densities for **(a)** CO and **(b)** H_2 production after 10 min CPE at various applied potentials. CPE conditions: 10 mL/min flow of CO_2 in a 0.1 M $CsHCO_3$ aqueous solution.
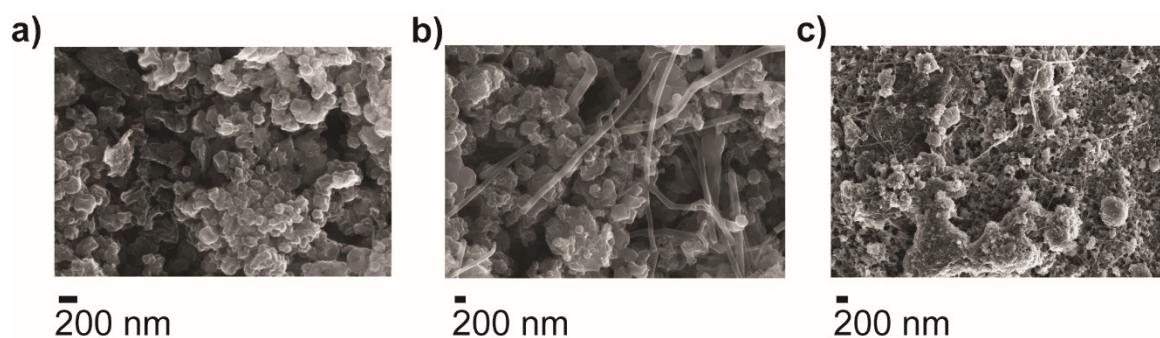

Figure S12. SEM images of **(a)** FeNC-rGO, **(b)** FeNC-CNF and **(c)** FeNC-CNT deposited on GDL, after 10 min CPE at various applied potentials. The materials have been characterized after the series of electrolysis reported in Figure S11. CPE conditions: 10 mL/min flow of CO_2 in a 0.1 M $CsHCO_3$
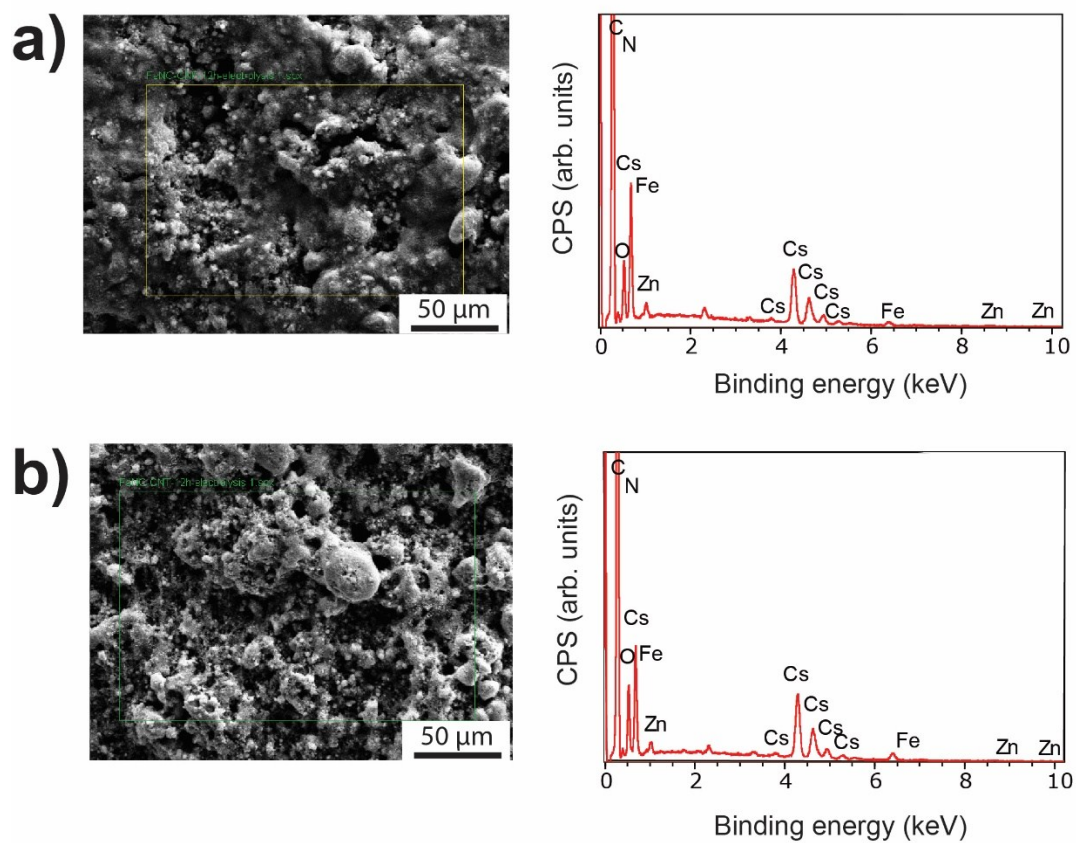
Figure S13. EDS analysis of **(a)** FeNC-CNF **(b)** FeNC-CNT deposited on GDL, after 12 hours CPE at -0.7 V vs RHE. CPE conditions: 10 mL/min flow of CO_2 in a 0.1 M $CsHCO_3$.

Table S1. Fe contents within the various electrodes determined using ICP-AES analysis of solutions prepared by hot-plate digestion of electrode materials in 5 ml of the H_2SO_4-HNO_3 (3:1) mixture and diluted 4 times with HNO_3. Fe amounts are expressed in ppm within the final solution.

	Wavelength (nm)	*Standard Deviation*	*Mass concentration of Fe (ppm)*	*Amount of Fe per 1 cm² (mg)*
FeNC alone	259.94	0.124	11.804	0.053
FeNC-rGO	259.94	0.056	12.68	0.063
FeNC-CNF	259.94	0.108	16.988	0.084
FeNC-CNT	259.94	0.168	11.764	0.058

Table S2. The Tafel parameters are the intercept, a, which is actually $\log(i_0)$, and the slope, b. Tafel parameters were determined by fitting the linear portion of the plot and the goodness of fit of the data to the model was evaluated by using the regression coefficient (R^2).

	Tafel Slope for CO (mV)	*Onset Potential for CO (mV)*	**Regression coefficient (R^2)**
FeNC alone	231	404	0.97526
FeNC-rGO	244	314	0.93551
FeNC-CNF	198	323	0.87841
FeNC-CNT	262	282	0.94627