Electronic Supplementary Material (ESI) for ChemComm.
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Catalytic CO_2-to-CO conversion in water by covalently functionalized carbon nanotubes with a molecular iron catalyst

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Supplementary Materials

Figure S1. Linear scan voltammetry (v = 0.01 V s^{-1}) of CAT_{CO2H} immobilized on MWCNTs in CO_2 saturated (0.038 M) H_2O (pH 7.3) + $NaHCO_3$ 0.5 M, showing the splitting of the Fe^{III}/Fe^{II} wave.

Figure S2. Current (black trace, left) and charge (red trace, right) during controlled potential electrolysis (E = −1.06 V vs. SHE) with TPP_{CO2H} covalently immobilized on MWCNTs (Γ = 2.0 10^{-9} mol cm^{-2}), in CO_2 saturated water (pH 7.3) + $NaHCO_3$ 0.5 M.

Figure S3. Gas chromatograms of (a) gases contained in the headspace of the electrolysis cell and (b) CO evolved during controlled potential electrolysis (- 1.06 V vs ENH) of $CATCO_2H$ immobilized on MWCNTs in CO_2-saturated H_2O + $NaHCO_3$ 0.5 M (pH 7.3).

Figure S4. (a) Current (black trace, left) and charge (red trace, right) during controlled potential electrolysis (E = −1.03 V vs. NHE) with unmodified MWCNTs, in CO_2 saturated water (pH 7.3) + $NaHCO_3$ 0.5 M, (b) Analysis of the products formed during electrolysis. Total faradaic efficiency was 25 %.

Figure S5. (a) Current (black trace, left) and charge (red trace, right) during controlled potential electrolysis (E = −1.03 V vs. NHE) with MWCNTs modified by covalent grafting of paraphenylmethyl amine, in CO_2 saturated water (pH 7.3) + $NaHCO_3$ 0.5 M, (b) Analysis of the products formed during electrolysis. Total faradaic efficiency was 24 %.

Figure S6. (a) Current (black trace, left) and charge (red trace, right) during controlled potential electrolysis (E = −1.03 V vs. NHE) with CAT_{CO2H} covalently immobilized on MWCNTs, in Ar purged water (pH 7.3) + $NaHCO_3$ 0.5 M, (b) Analysis of the products formed during electrolysis. Total faradaic efficiency was 11 %.

Figure S7. XPS spectra of (a) GC/CNTs/Diazonium/CAT_{CO2H} and (b) GC/CNTs/Diazonium in the Cl2p region.

1. Chemicals

All starting materials were obtained from Sigma-Aldrich, Fluka, or Alfa Aesar, and used without further purification. 1-pyrenebutanal was synthesized according to a literature procedure.[S1] $CHCl_3$ and CH_2Cl_2 were distilled from calcium hydride and stored under an argon atmosphere. N,N'-dimethylformamide was obtained from Acros (>99.8%, over molecular sieves). NBu_4BF_4 was obtained from Fluka (puriss.) and used without further purification. ^{1}H NMR spectra were recorded on a Bruker Avance III 400-MHz spectrometer and were referenced to the resonances of the solvent used.

Synthesis of 4-(N-Boc-aminomethyl)benzene diazonium tetrafluoroborate salt

Following a literature procedure[1], *tert*-butyl 4-(aminobenzyl)carbamate (1 eq.) was dissolved in HBF_4 (48 %) and water (0.3:1) and the solution was cooled to 0° C. A cold solution of sodium nitrite (1.1 eq.) was added to the solution under Ar. The reaction mixture was stirred at 0° C for 20 minutes. A white precipitate formed, and was filtered and washed with Et_2O. The orange residue was dried under vacuum (50 % yield).

^{1}H NMR (400 MHz, CD_3CN) δ 8.41 (d, 2H, Ar*H*) 7.79 (d, 2H, Ar*H*) 6.07 (bs, 1H, N*H*) 4.43 (d, 2H, C*H$_2$*) 1.42 (s, 9H, ^{t}Bu)

Synthesis of 5,10,15-tris(2,6-dimethoxyphenyl)-20-(4-carboxymethylphenyl) porphyrin – A_3B_{CO2Me}

2,6-dimethoxybenzaldehyde (3 eq.) and methyl-4-formylbenzoate (1 eq.) were dissolved in $CHCl_3$. The solution was degassed with Ar for 15 min. Pyrrole (4 eq.) was added and the reaction mixture protected from light. $BF_3.Et_2O$ (1.1 eq.) was then added and the reaction mixture was stirred at room temperature, under Ar, for 1 hour. 2,3-dichloro-5,6-dicyanobenzoquinone (3.7 eq.) was added to the dark purple solution, and the reaction mixture stirred at room temperature overnight. Triethylamine (1.1 eq.) was added and the reaction mixture stirred for an additional 30 min. The mixture was filtered over a pad of silica, and eluted with CH_2Cl_2. The solvents were removed under reduced pressure and the crude mixture of porphyrins was finally purified by column chromatography on silica ($CHCl_3$/EtOAc, 9 :1). A purple solid was isolated (7 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.71 (m, 8H, H_{pyrrole}) 8.40 (d, 2H, $\mathrm{Ar_{CO2Me}}H_{\mathrm{meta}}$) 8.30 (d, 2H, $\mathrm{Ar_{CO2Me}}H_{\mathrm{ortho}}$) 7.70 (2t, 3H, $\mathrm{Ar_{dimethoxy}}H_{\mathrm{para}}$) 6.98 (2d, 6H, $\mathrm{Ar_{dimethoxy}}H_{\mathrm{meta}}$) 4.10 (s, 3H, $\mathrm{-CO_2C}H_3$) 3.50 (2s, 18H, $\mathrm{-OC}H_3$) -2.55 (bs, 2H, N*H*) ; **^{13}C NMR** (100 MHz, CDCl3) *δ* 167.70 160.78 147.93 134.70 130.19 129.27 127.81 120.36 120.17 117.40 111.85 111.35 104.47 104.40 56.24 52.40 ; **HRMS** [M+H]+ Calculated for C52H44N4O8 853.32 Found 853.31

Synthesis of 5,10,15-tris(2,6-dimethoxyphenyl)-20-(4-carboxyphenyl) porphyrin - A_3B_{CO2H}

A_3B_{CO2Me} (1 eq.) was dissolved in a mixture of THF, EtOH, and 2 M KOH (2 :1 :2), and stirred overnight under Ar, at room temperature. The organic solvents were removed under reduced pressure, and the mixture was acidified with 1 M HCl. The porphyrin was extracted with CH_2Cl_2, and the green organic phase was washed with water and brine, until a purple solution was obtained. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. A purple solid was isolated (100 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.72 (m, 8H, H_{pyrrole}) 8.46 (d, 2H, $\mathrm{Ar_{CO2H}}H_{\mathrm{meta}}$) 8.34 (d, 2H, $\mathrm{Ar_{CO2H}}H_{\mathrm{ortho}}$) 7.72 (2t, 3H, $\mathrm{Ar_{dimethoxy}}H_{\mathrm{para}}$) 7.00 (2d, 6H, $\mathrm{Ar_{dimethoxy}}H_{\mathrm{meta}}$) 3.52 (2s, 18H, $\mathrm{-OC}H_3$) -2.54 (bs, 2H, N*H*) ; **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 160.37 148.37 135.19 134.88 130.39 128.59 127.98 119.43 103.55 102.19 56.17 ; **HRMS** [M+H]+ Calculated for C51H42N4O8 839.30 Found 839.43

Synthesis of 5,10,15-tris(2,6-dihydroxyphenyl)-20-(4-carboxyphenyl) porphyrin - A'_3B_{CO2H}

A_3B_{CO2H} (1 eq.) was dissolved in freshly distilled CH_2Cl_2 (10 mL) and the solution was cooled to -20°C, and degassed under Ar. A 1 M solution of BBr_3 (30 eq.) was slowly added to the reaction mixture, and the resulting green mixture was stirred at -20°C for 1h. The reaction mixture was then stirred overnight at room temperature. The solution was diluted with ethyl acetate (100 mL). The organic phase was washed with saturated $NaHCO_3$ (2x50 mL), water (2x50 mL) and brine (2x50 mL). The organic phase was further dried with $MgSO_4$, and brought to dryness under reduced pressure. A purple solid was isolated (100 % yield).

^{1}H NMR (400 MHz, d_6-DMSO) *δ* 13.22 (bs, 1H, $\mathrm{CO_2}H$) 9.27 (s, 6H, -O*H*) 8.77 (m, 8H, H_{pyrrole}) 8.35 (m, 4H, $\mathrm{Ar_{CO2H}}H_{\mathrm{ortho/meta}}$) 7.40 (2t, 3H, $\mathrm{Ar_{dihydroxy}}H_{\mathrm{para}}$) 6.79 (2d, 6H, $\mathrm{Ar_{dihydroxy}}H_{\mathrm{meta}}$) -2.82 (bs, 2H, N*H*) ; **HRMS** [M+H]+ Calculated for C45H30N4O8 755.21 Found 755.18

Synthesis of Iron(III) Chloride 5,10,15-tris(2,6-dihydroxyphenyl)-20-(4-carboxyphenyl) porphyrin - CAT_{CO2H}

A'_3B_{CO2H} (1 eq.) was dissolved in freshly distilled MeOH (10 mL), and the solution was degassed under Ar. $FeBr_2$ (18 eq.) and 2,6-lutidine (2.5 eq.) were added to the solution. The reaction mixture was stirred overnight at 60°C. The solution was diluted with ethyl acetate (100 mL), and 1 M HCl was added. The organic phase was washed with 0.1 M HCl (2x50 mL), water (2x50 mL) and brine (2x50 mL). The organic phase was dried with $MgSO_4$, and brought to dryness under reduced pressure. A dark purple solid was isolated (98 % yield).

HRMS [M]+ Calculated for C45H28FeN4O8 808.13 Found 808.42

Synthesis of 5,10,15-triphenyl-20-(4-carboxymethylphenyl)porphyrin – TPP_{CO2Me}

Following a literature procedure,[2] benzaldehyde (3 eq.) and methyl-4-formylbenzoate (1eq.) were dissolved in $CHCl_3$, and the solution was degassed for 15 min. Pyrrole (4 eq.) was added and the reaction mixture protected from light. $BF_3.Et_2O$ (1.1 eq.) was then added and the reaction mixture was stirred at room temperature, under Ar, for 1 hour. 2,3-dichloro-5,6-dicyanobenzoquinone (3.7 eq.) was added to the dark purple solution, and the reaction mixture was stirred at room temperature overnight. Triethylamine (1.1 eq.) was added and the reaction mixture stirred for an additional 30 min. The mixture was filtered over a pad of silica, and eluted with CH_2Cl_2. The solvents were removed under reduced pressure and the crude mixture of porphyrins was finally purified by column chromatography on silica ($CHCl_3$/EtOAc, 95:5). A purple solid was isolated (16 % yied).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (m, 8H, $H_{pyrrole}$) 8.44 (d, 2H, $Ar_{CO2Me}H_{meta}$) 8.31 (d, 2H, $Ar_{CO2Me}H_{ortho}$) 8.22 (m, 6H, Ph*H*) 7.76 (m, 9H, Ph*H*) 4.11 (s, 3H, $-CO_2CH_3$) -2.77 (bs, 2H, N*H*) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5 147.1 142.2 134.7 134.7 131.4 128.1 127.9 126.9 120.5 118.7 52.6

Synthesis of 5,10,15-triphenyl-20-(4-carboxyphenyl)porphyrin – TPP_{CO2H}

TPP_{CO2Me} (1 eq.) was dissolved in a mixture of THF, EtOH, and 2 M KOH (2:1:2), and stirred overnight, under Ar, at room temperature. The organic solvents were removed under reduced pressure, and the mixture was acidified with 1 M HCl. The porphyrin was extracted with CH_2Cl_2, and the green organic phase was washed with water and brine until a purple solution was obtained. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford a purple solid in quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (m, 8H, $H_{pyrrole}$) 8.52 (d, 2H, $Ar_{CO2H}H_{meta}$) 8.32 (d, 2H, $Ar_{CO2H}H_{ortho}$) 8.22 (m, 6H, Ph*H*) 7.76 (m, 9H, Ph*H*) -2.77 (bs, 2H, N*H*) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.7 146.5 141.9 134.4 130.7 127.9 127.6 126.6 120.4 120.2 118.7

Synthesis of Iron(III) Chloride 5,10,15-triphenyl-20-(4-carboxyphenyl)porphyrin – $FeTPP_{CO2H}$

TPP_{CO2H} (1 eq.) was dissolved in freshly distilled THF. $FeBr_2$ (18 eq.) and 2,6-lutidine (5 eq.) were added, and the reaction mixture was stirred at reflux, under Ar, overnight. The solvent was removed under reduced pressure, and the crude was dissolved in $CHCl_3$. The organic phase was washed with 0.1 M HCl (2x100 mL), water (2x100 mL) and brine (2x100 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. A dark purple solid was isolated (90 % yield).

Immobilization of 4-(N-Boc-aminomethyl)benzene on carbon nanotubes

Multi-walled carbon nanotubes (100 mg) were suspended in a 10 mM solution of 4-(N-Boc-aminomethyl)benzene diazonium tetrafluoroborate salt in acetonitrile, and stirred at 85° C overnight. The modified nanotubes were centrifuged (12000 rpm, 15 minutes), sequentially washed with ethanol and acetone, and dried under vacuum.

Deprotection of the modified carbon nanotubes

The removal of the Boc protecting group was achieved by suspending the modified carbon nanotubes in MeOH/HCl 4 M and stirring at room temperature for 1h30. The deprotected nanotubes were centrifuged (12000 rpm, 15 minutes), washed sequentially with water, ethanol and acetone, and dried under vacuum.

Coupling with the iron porphyrin catalysts

The deprotected carbon nanotubes were suspended in a 10 mM solution of the catalyst in DMF, under Ar. HBTU (12 mM) and DIPEA (20 mM) were added to the solution, and the reaction mixture was stirred at room temperature, under Ar, overnight. The nanotubes were centrifuged (12000 rpm, 15 minutes), washed sequentially with DMF, ethanol and acetone until the supernatant was colorless, and dried under vacuum.

2. Methods and Instrumentation.

Cyclic Voltammetry. Cyclic voltammetry experiments were performed using an AUTOLAB PGSTAT128N potentiostat (Metrohm). The three-electrodes setup consisted of a glassy carbon working electrode (custom made, 0.071 cm^2) polished with diamond paste of various diameter size (successively 15, 6, 3, and 1 µm, 60 seconds each), a Pt wire counter electrode, and a SCE reference electrode (-0.241 V vs NHE). All experiments were performed under Argon or CO_2 atmosphere at 25°C, the double-wall jacketed cell being thermostated by circulation of water. Ohmic drop was compensated using the positive feedback compensation implemented in the instrument.

Preparative Scale Electrolysis. Controlled potential electrolyses were performed using a PARSTAT 4000 potentiostat (Princeton Applied Research). The experiments were carried out in a cell using a glassy carbon plate (S = 2.5 cm^2) as working electrode, and a SCE reference electrode. The Pt grid counter electrode was separated from the cathodic compartment with a glass frit.

Preparation of the electrodes

For cyclic voltammetry experiments, a glassy carbon electrode (0.071 cm^2) was polished with diamond paste (successively 15, 6, 3, and 1 µm, 60 seconds each), thoroughly rinsed and sonicated in ethanol, and dried. Modified multiwalled carbon nanotubes (CNTs/Diazonium/CAT$_{CO2H}$) were dispersed in 2-propanol (iPrOH, 1 mg mL^{-1}) by sonication (15 minutes), 10 µL of the suspension were dropped on the surface of the electrode, and allowed to dry under ambient conditions. The electrodes were rinsed with iPrOH and allowed to dry under ambient conditions before the experiments.

For controlled potential electrolyses, a glassy carbon plate (2.5 cm^2) was polished with diamond paste (successively 15, 6, 3, and 1 µm, 60 seconds each), thoroughly rinsed and sonicated in ethanol, and dried. Modified multiwalled carbon nanotubes (CNTs/Diazonium/CAT$_{CO2H}$) were dispersed in 2-propanol (iPrOH, 1 mg mL^{-1}) by sonication (15 minutes). 150 µL of the suspension were dropped on each face of the electrode, and allowed to dry under ambient conditions. The electrodes were rinsed with iPrOH and allowed to dry under ambient conditions before the experiments.

Determination of Porphyrin surface coverage

The surface concentration of electroactive species was determined by integrating the current of the Fe(III)/Fe(II) wave, and applying the following equation relating the charge passed to the surface concentration :

$$\Gamma = \frac{Q}{nFA}$$

where Γ is the surface concentration in electroactive species (mol cm^{-2}), Q is the charge obtained from the integration of the electrochemical wave (C), n is the number of electrons exchanged (here, 1 electron), F is the Faraday constant (96485 C mol^{-1}) and A is the electrode surface (cm^2).

Gas Detection. Gas chromatography analyses of gas evolved in the headspace during the electrolysis were performed with an Agilent Technologies 7820A GC system equipped with a thermal conductivity detector. CO and H_2 production was quantitatively detected using a CP-CarboPlot P7 capillary column (27.46 m in length and 25 µm internal diameter). Temperature was held at 150 °C for the detector and 34 °C for the oven. The carrier gas was argon flowing at 9.5 mL/min at constant pressure of 0.5 bars. Injection was performed via a 250-µL gas-tight (Hamilton) syringe previously degassed with CO_2. Conditions allowed detection of H_2, O_2, N_2, CO, and CO_2. Calibration curves for H_2 and CO were determined separately by injecting known quantities of pure gas.

SEM analysis. Scanning electron microscopy using a field emission gun (SEM-FEG) was performed using a Zeiss Supra 40.

XPS analysis. An X-Ray Photoelectron Spectrometer THERMO-VG ESCALAB 250 (RX source K Al (1486.6 eV)) was used.

3. Additional figures

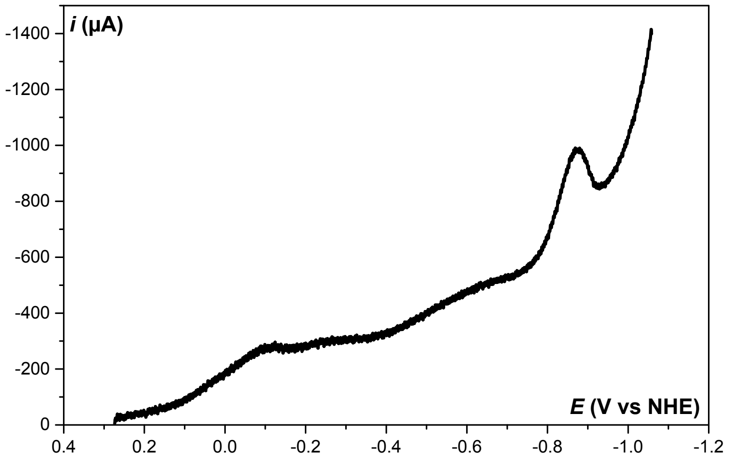

Figure S1. Linear scan voltammetry (v = 0.01 V s^{-1}) of CAT$_{CO2H}$ immobilized on CNTs in CO_2 saturated (0.038 M) H_2O (pH 7.3) + $NaHCO_3$ 0.5 M, showing the splitting of the Fe^{III}/Fe^{II} wave.

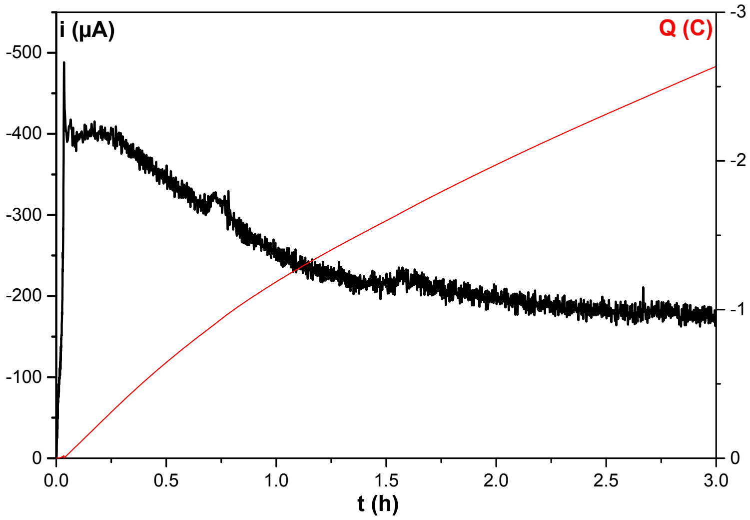

Figure S2. Current (black trace, left) and charge (red trace, right) during controlled potential electrolysis (E = −1.06 V vs. NHE) with TPP_{CO2H} covalently immobilized on MWCNTs (Γ = 2.0 10^{-9} mol cm^{-2}), in CO_2 saturated water (pH 7.3) + $NaHCO_3$ 0.5 M.

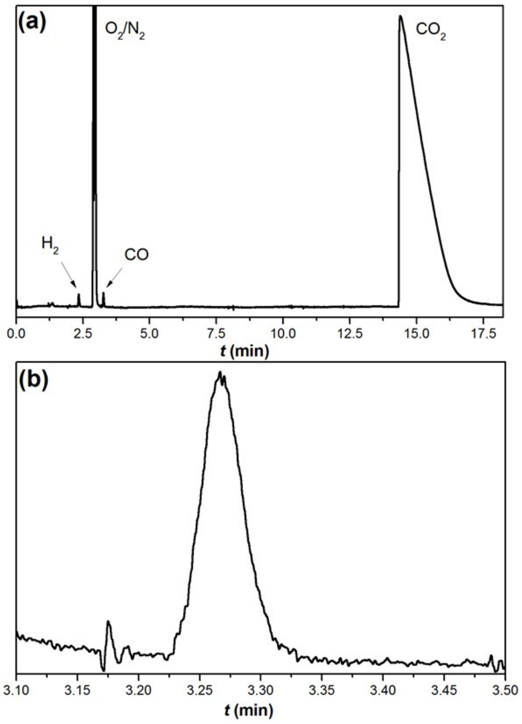

Figure S3. Gas chromatograms of (a) gases contained in the headspace of the electrolysis cell and (b) CO evolved during controlled potential electrolysis (- 1.06 V vs NHE) of CAT_{CO2H} immobilized on MWCNTs in CO_2-saturated H_2O + $NaHCO_3$ 0.5 M (pH 7.3).

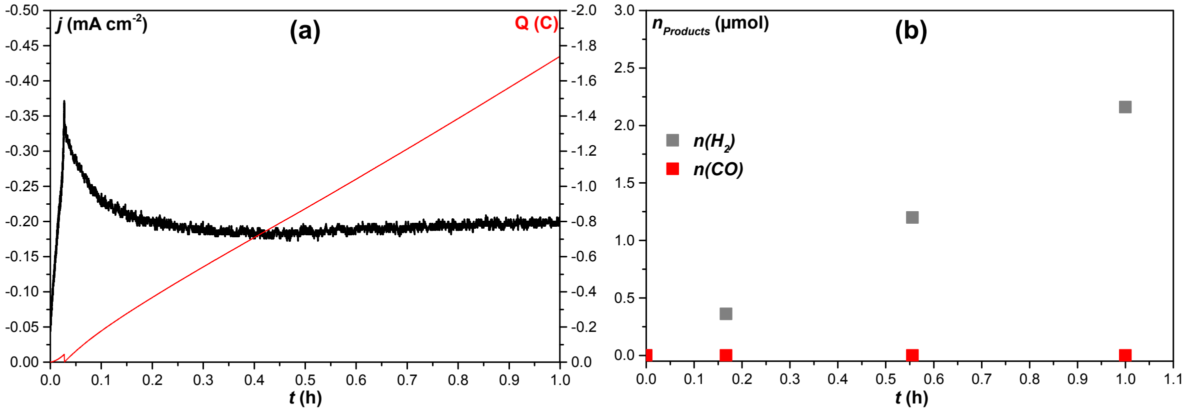

Figure S4. (a) Current (black trace, left) and charge (red trace, right) during controlled potential electrolysis (*E* = −1.03 V vs. NHE) with unmodified MWCNTs, in CO_2 saturated water (pH 7.3) + $NaHCO_3$ 0.5 M, (b) Analysis of the products formed during electrolysis. Total faradaic efficiency was 25 %.

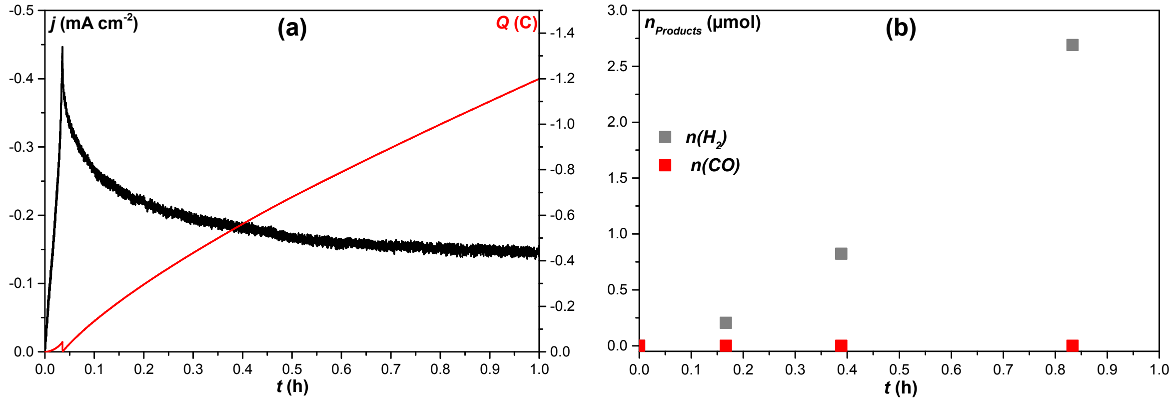

Figure S5. (a) Current (black trace, left) and charge (red trace, right) during controlled potential electrolysis (*E* = −1.03 V vs. NHE) with MWCNTs modified by covalent grafting of paraphenylmethyl amine, in CO_2 saturated water (pH 7.3) + $NaHCO_3$ 0.5 M, (b) Analysis of the products formed during electrolysis. Total faradaic efficiency was 24 %.

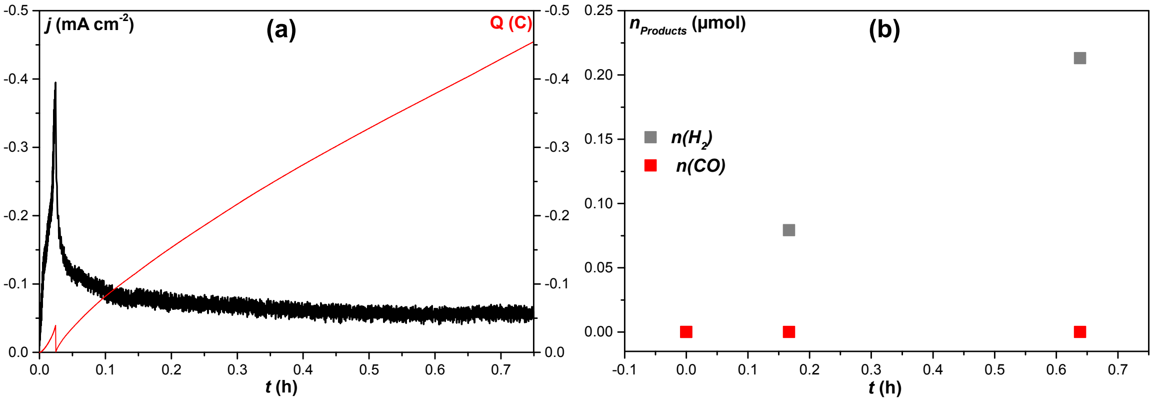

Figure S6 (a) Current (black trace, left) and charge (red trace, right) during controlled potential electrolysis (*E* = −1.03 V vs. NHE) with CAT_{CO2H} covalently immobilized on MWCNTs, in Ar purged water (pH 7.3) + $NaHCO_3$ 0.5 M, (b) Analysis of the products formed during electrolysis. Total faradaic efficiency was 11 %.

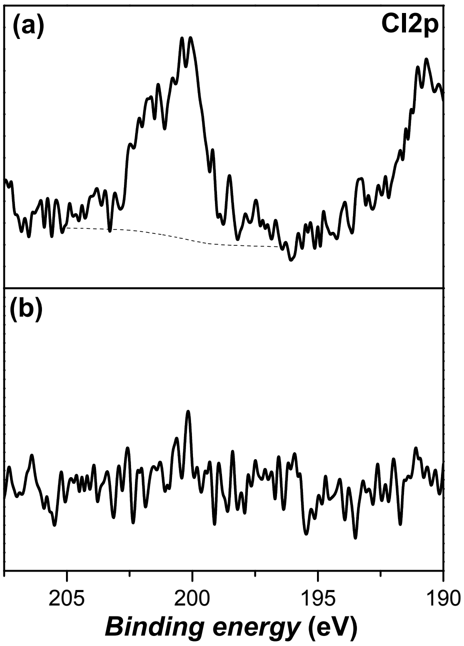

Figure S7. XPS spectra of (a) GC/CNTs/Diazonium/CAT$_{CO2H}$ and (b) GC/CNTs/Diazonium in the Cl2p region.

References

1. J. M. Chretien, M. A. Ghanem, P. N. Bartlett and J. D. Kilburn, *Chemistry*, 2008, **14**, 2548-2556.
2. M. Tanasova and B. Borhan, *European Journal of Organic Chemistry*, 2012, **2012**, 3261-3269.