

Molecular Engineering of a Cobalt-based Electrocatalytic Nano-Material for H₂ Evolution under **Fully** Aqueous Conditions

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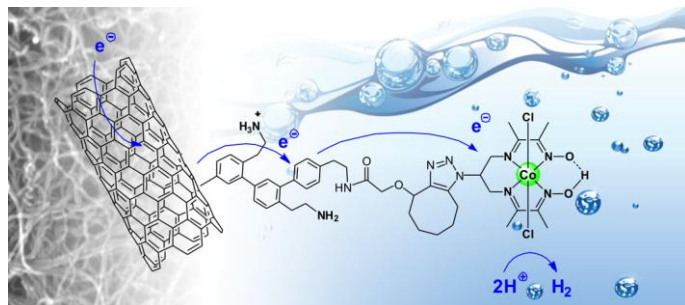
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TOC graphic



TOC summary :

Efficient hydrogen evolving catalysts comprised of readily available elements are needed if hydrogen is to be adopted as a clean alternative to fossil fuels. Now, the covalent attachment of a diimine-dioxime cobalt complex to carbon nanotubes yields an active and robust electrocatalyst for hydrogen generation (55000 TON in 7 hours) from aqueous solutions at mild overpotentials.

Abstract:

The viability of a hydrogen economy depends on the design of efficient catalytic systems based on earth-abundant elements. Innovative breakthroughs for hydrogen evolution based on molecular tetraimine cobalt compounds appeared in the past decade. Here we show that such a diimine-dioxime cobalt catalyst can be grafted at the surface of an electrode made of carbon nanotubes. The resulting electrocatalytic cathode material mediates H₂ generation (55000 TON in 7h) from fully aqueous solutions at low to medium overpotentials. This material is remarkably stable, allowing extensive cycling with preservation of the grafted molecular complex as shown from electrochemical, X-ray photoelectron spectroscopy and scanning electron microscopy. This clearly indicates that grafting provides a largely increased stability to these cobalt catalysts, and suggests the possible application of these materials in the development of technological devices.

Keywords:

hydrogen evolution, electrocatalysis, molecular materials, cobalt, carbon nanotubes

In the context of increased global energy demand and continuous depletion of fossil fuel reserves, the exploitation of renewable carbon-neutral energy sources such as sunlight is one of the greatest scientific challenges of this century.¹ As their availability does not strictly meet the demand, energy from renewable sources must however be stored durably for further use. The production of hydrogen through water-splitting, either electrochemically or photochemically, appears as a promising and sustainable solution to store energy in a chemical and stable form, before converting it back to electricity, for example in a hydrogen-driven fuel cell.² Electrocatalysis is the key enabling technology for these processes.³ However precious metals, namely platinum, are often used for H₂-related applications although they are neither cheap nor sustainable resources.⁴ There is thus a crucial need for designing efficient systems based on earth-abundant first row transition metals, capable of producing H₂ from water with high catalytic activity and stability.

Innovative breakthroughs based on cobalt compounds appeared in the past decade^{5,6} for both hydrogen evolution and water oxidation reactions.⁷⁻¹¹ Notably, we^{12,13} and others^{14,15} reported that a series of cobaloxime compounds displays remarkable properties for proton reduction in non-aqueous solvents with low overpotential requirements.¹⁶ Practical

applications of such molecular catalysts require however their incorporation in electrode materials that can operate with **fully** aqueous electrolytes, as previously demonstrated with DuBois' nickel-based system.¹⁷⁻¹⁹ In these studies and others involving water oxidation catalysts,²⁰⁻²² carbon nanotubes (CNTs) were chosen as electrode materials for the following reasons: they first provide large surface areas and thus high catalyst loading;²³ second, electrodes based on CNTs display remarkable properties in terms of stability and electronic conductivity,^{24,25} third, versatile and straightforward methods,²⁶ such as electroreduction of functionalized aryldiazonium salts,²⁷ are available for grafting molecular complexes onto various carbon materials such as CNTs. As a first step towards this goal, we recently reported²⁸ on a second generation of cobalt H₂-evolving catalysts based on a tetradentate diimine-dioxime ligand that display excellent catalytic properties (in terms of overpotential requirement and turnover frequencies) combined with greater stabilities compared to the previously reported cobaloximes. Here we show that these second-generation catalysts can be used for the molecular engineering of a H₂-evolving cathode material working in a purely aqueous electrolyte at small to moderate overpotentials and mild pH. The retention of the catalytic activity upon grafting also allows deriving conclusions about the **heterolytic** nature of the H₂-evolving step, still under debate for this class of catalysts.⁵

Results and discussion

Derivatization of diimine-dioxime cobalt catalyst. Cobaloxime compounds can only be covalently functionalized at the substituent of the glyoxime ligand. Due to the innate reactivity of these complexes, ligand modification has to be achieved before assembly of the complex, leading to undesired symmetrical poly-functionalized complexes. By contrast cobalt diimine-dioxime complexes are well-suited for a selective mono-functionalization on the C3 hydrocarbon chain of the tetradentate diimine-dioxime (DOH)₂pn ligand: an azido group can be introduced in a straightforward manner thanks to its inertness under the harsh conditions required for the bis-ketimine condensation. In addition, azido groups selectively react with various alkyne-containing substrates via azide-alkyne cycloaddition (the most famous reaction in click chemistry)²⁹ under smooth conditions, usually compatible with most organic and metallorganic functions.

The azido-functionalized diimine-dioxime ligand **1** is prepared from commercially available 2-hydroxy-1,3-diaminopropane in 5 steps (see the full synthetic protocol in the Supplementary Information). Reaction of **1** with Co(II) chloride in the presence of air leads to the pure [Co^{III}(DO)(DOH)N₃-pnCl₂] complex **2** in very good yield. The molecular structure of

the complex was solved by X-ray crystal diffraction (Figure 1) and shows an octahedral environment around the cobalt(III) ion with two axial chloride ligands located in *trans* positions.

Fabrication of carbon nanotube electrodes. Standard copper-catalyzed conditions for the azide-alkyne cycloaddition reaction resulted into substitution of the cobalt ion by a copper one. We then used Bertozzi's copper-free click methodology based on a strained functionalized cyclooctyne³⁰ to attach the azido derivative **2** onto an electrode containing amino-functionalized multi-walled carbon nanotubes¹⁸ (MWCNTs, Figure 1). We first prepared the *N*-hydroxyphthalimide activated ester of 2-(cyclooct-2-yn-1-yloxy)ethanoic acid and clicked it with **2** so as to yield the cobalt(III) complex **3**, which was isolated and purified. Cyclic voltammograms in the presence of anilinium tetrafluoroborate in acetonitrile (Supplementary Figure S1) and bulk electrolysis experiments show that **3** is active for electrocatalytic H₂ evolution with an overpotential requirement of 185 mV, significantly lower than the non-substituted [Co(DO)(DOH)pnBr₂] complex (290 mV).¹⁶ Using the catalytic current enhancement, expressed as the i_c/i_p ratio with i_c the catalytic current and i_p the peak current associated with the Co(II/I) couple, as a proxy for the catalytic turnover frequency, we note that **3** is a slower catalyst as compared to **2** (Supplementary Figure S2), as already observed for nickel catalysts.¹⁸ **This clearly indicates that flexibility at the propylene bridge promotes reorganisation around Co while cycling through various oxidation states during hydrogen evolution.**

In parallel, a mixture of Nafion® and MWCNTs was deposited on a gas diffusion layer (GDL) electrode. Then the MWCNTs were decorated with a poly-4-(2-aminoethyl)phenylene layer as schematically represented in Figure 1 through the electroreduction of the corresponding aryldiazonium salt, as previously described.²³ Cobalt complex **3** was finally covalently attached to the electrode under smooth conditions through amide linkages generated during reaction of the activated ester of **3** with the grafted amine residues in CH₂Cl₂ at room temperature and in the presence of 2,6-lutidine. A schematic representation of the resulting functionalized CNT/Co material is displayed in Figure 1.

Characterization of the electrode material. Figure 2 shows the cyclic voltammogram recorded for the functionalized electrode. Comparison with that measured for bulk **3** at a similar but unfunctionalized GDL/MWCNT electrode in CH₃CN clearly indicates that the structure of the cobalt complex has been retained upon grafting: Both display a well-defined reversible process at -1.08 V *versus* Fc⁺/Fc assigned to the Co(II)/Co(I) couple of the

complex.³¹ In the case of the functionalized material, the reversibility of the Co(III)/Co(II) process, associated with chloride elimination from the Co(III) center, can be partially resolved near -0.6 V *versus* Fc⁺/Fc only if a concentrated chloride solution is used as the electrolyte. Only the Co(II)/Co(I) process is seen in the absence of chloride anions in solution (Supplementary Figure S9). The intensities of both anodic and cathodic peaks of the Co(II)/Co(I) system are directly proportional to the scan rate (Supplementary Figure S3) confirming the immobilization of the cobalt complexes onto the electrode surface. Surface catalyst concentration as high as $4.5 (\pm 0.2) \times 10^{-9}$ mol·cm⁻² could be estimated from the integration of this mono-electronic wave (Figure 2). The indicated error accounts for the dispersion of results measured at different scan rates and on 5 distinct samples. XPS analysis (Figure 3 and Supplementary Figure S4) nicely confirmed the presence of the diimine-dioxime cobalt complex at the surface of the electrode. By comparison to the spectrum of amino-decorated MWCNTs (red trace in Figure 3; note that nitrogen is not detected in the black trace of pristine MWCNTs), the XPS analysis of the CNT/Co sample (blue trace, Supplementary Table S1) shows an increase in the nitrogen peak intensity as well as two sharp peaks in the Co region with binding energies of 781.7 eV and 796.6 eV corresponding to the 2p_{3/2} and 2p_{1/2} levels in a 2:1 ratio. The difference of 14.9 eV between the peaks as well as the absence of shake-up satellite on Co_{2p} core level signals clearly evidence the presence of the Co(III) ion. Considering that the peak obtained at 284.4 eV in the decomposition of C 1s energy level signal with three Gaussian-Lorentzian curves³² corresponds mainly to the electrons collected from the sp² carbons of the CNTs the calculation of the intensity ratio Co2p_{3/2}/C1s allows to estimate about one cobalt atoms for 310 carbons (Supplementary Figure S5).

The scanning electron micrograph (SEM) of the CNT/Co electrode (Supplementary Figure S6) shows the homogeneous deposit of carbon nanotubes and confirms the absence of large conglomerates or nanoparticles following derivatization.

Catalytic hydrogen evolution. Catalytic H₂ evolution mediated by diimine-dioxime cobalt complexes has only been observed in non-aqueous solvents so far.^{28,33} In the following we will show that the new molecular-based CNT/Co material is catalytically competent for H₂ evolution from fully aqueous electrolytes at mild pH. We first ran a linear sweep voltammetry experiment recorded on a CNT/Co electrode (Figure 4a blue solid trace) in acetate buffer solution (0.1 M, pH 4.5). N₂ was continuously bubbled through the electrolyte at a constant flow during the experiment and the output gas was analyzed every 2 min by gas

chromatography (see the Supplementary Information). H₂ could be detected by gas chromatography starting from -0.35 V *versus* RHE (350 mV onset overpotential, blue dotted trace), which compares well with the overpotential requirement (290 mV) determined for [Co(DO)(DOH)pnBr₂] in CH₃CN.¹⁶ An overpotential value of 590 mV is required to reach a current density value of 1 mA·cm⁻². By comparison, unfunctionalized GDL/MWCNT electrodes (black traces in Figure 4a) display a much lower catalytic H₂-evolution activity. Tafel analysis (Supplementary Figure S10) gives a Tafel slope of 160 mV/decade and exchange current density of 10^{-6.5} A·cm⁻²_{geometric}. This value is comparable with that reported for electrodeposited MoS₂ catalysts (10^{-6.5} A·cm⁻²_{geometric}).³⁴ For comparison, NiMo-based materials exhibit current densities between 10⁻⁶ and 10^{-3.5} A·cm⁻²_{geometric}.^{35,36}

Material stability and mechanistic insights. For catalytic stability assessment, the electrode has then been poised at a constant potential of -0.59 V *versus* RHE in acetate buffer. As shown in Figure 4b, the current density stabilizes after about one hour at a constant value of approx. 1 mA·cm⁻². Considering that 2e⁻ are required for the formation of a H₂ molecule and using the above determined surface concentration of the catalyst (4.5 (± 0.2) × 10⁻⁹ mol·cm⁻²) we could calculate a turnover frequency per grafted Co catalyst of ~8000 (± 5%) h⁻¹. Over a 4h-experiment and after subtraction of the control experiment, a turnover number of 33000 (± 5%) could be determined with a near-quantitative faradaic yield (0.97 ± 0.05). During a longer experiment, 55000 (± 5%) turnovers were performed in 7 hours with a similar faradaic efficiency. These values compare well with those obtained when other nickel-based H₂-evolving catalysts have been grafted on MWCNTs through similar methods.^{18,19}

Remarkably, the stability of the present molecular catalyst is enhanced by several orders of magnitude after immobilization on the electrode, since previous solution studies for [Co(DO)(DOH)pnBr₂] showed significant degradation after 50 turnovers.²⁸ Though no detailed “post-mortem” analysis has been reported yet for cobaloxime or diimine-dioxime catalysts, a recent report on related diimine-dipyridine metal complexes³⁷ shows that reductive processes at the metal site may generate transient carbon-based α-imino radical species that can undergo reductive homocoupling yielding dimer complexes with new metal coordination spheres likely not suitable for catalysis. Once grafted on electrode materials the molecular complexes are isolated and may not be able to react in such bimolecular manner. Additionally, the supply of electrons from CNTs to the catalyst is optimized in the CNT/Co material which should significantly limit the lifetime of reduced intermediates along the catalytic cycle and consequently avoid degradative side reactions. We believe that these are

the two main crucial reasons for the enhanced stability observed upon surface attachment as compared to homogeneous studies. Grafting thus provides an avenue for taking full benefit from the redox non-innocence of coordinated ligands for the design of active molecular electrocatalysts.

Another exciting observation was that the surface of the electrode after an electrolysis experiment did not show any alteration of the grafted complex. XPS measurements indeed reveal the same surface composition (Supplementary Figure S8). In the Co region, the two broad sets of signals corresponding to the $2p_{3/2}$ and $2p_{1/2}$ core levels are still observed. The absence of any peak below 780.9 eV excludes the presence of cobalt oxide or metallic cobalt on the surface. SEM images (Supplementary Figure S6) are indistinguishable from those recorded immediately after derivatization. Cyclic voltammograms recorded in CH_3CN (Supplementary Figure S9) shows that the signal of the Co(II)/Co(I) couple of the grafted complex remains unchanged both in position and intensity. Thus we rule out the formation of reactive metallic or metal oxide particles and assign the catalytic activity exclusively to the intact grafted molecular complex. In addition, no H_2 evolution activity could be detected when the CNT/Co material was assayed in aqueous phosphate buffer (pH 7, Supplementary Figure S7), probably because the grafted molecular catalysts requires a more acidic environment for cycling. This observation thus clearly excludes any reductive transformation of the grafted molecular complex into the nanoparticulate H_2 -CoCat material that we recently reported and that would spontaneously form under these conditions if the molecular complex was free in solution.³⁸ This is a quite unique situation if one refers to the frequent reports that such particles, derived from the decomposition of molecular catalysts in solution³⁸⁻⁴² or heterogeneized,^{44,45} are in fact at least partly⁴³ responsible for catalysis.

It is thus the first time that a molecular and mononuclear cobalt complex is grafted at the surface of an electrode and found to be catalytically active. This allows deriving some conclusions regarding the mechanism at work during catalysis, an issue thoroughly discussed in the past five years in the case of cobaloxime catalysts.^{5,6} Two distinct mechanisms have been considered for catalysts in solution, both involving a metal-hydride species as the key intermediate: (i) in the homolytic mechanism, two metal-hydride complexes evolve H_2 through a reductive elimination reaction; (ii) in the alternative heterolytic pathway, the intermediate metal hydride species decomposes by proton attack and evolves H_2 via an intermediate dihydrogen complex. At the surface of an electrode two distinct immobilized centers are unlikely to react together, which rules out the homolytic mechanism. Further mechanistic studies are still needed to definitively assign the oxidation state of the active

species during catalysis, in line with recent theoretical studies on cobaloxime catalysts favoring Co(II)-H over Co(III)-H species in the heterolytic pathway.^{44,45}

Conclusions

Tetraimine cobalt complexes are among the most efficient molecular catalysts for H₂ evolution. We demonstrate here for the first time the successful integration of such a diiminedioxime cobalt catalyst coupled to carbon nanotubes into a very active electrocatalytic cathode material for H₂ generation from **fully** aqueous solutions from 325 mV overpotential. Around 55000 turnovers are obtained during 7 hours of electrolysis in acetate buffer at a potential of -0.59 V *versus* RHE. This material is remarkably stable, allowing extensive cycling with no alteration of the grafted molecular complex. This clearly indicates that grafting provides a largely increased stability to these cobalt catalysts, thus paving the way towards their development in technological devices.

Methods

Solvents and starting materials were purchased from Sigma-Aldrich and used without further purification, unless otherwise stated. When necessary, solvents were distilled under argon: diethylether was distilled by refluxing over Na/benzophenone; dry acetonitrile and dichloromethane were obtained by distillation on CaH₂. The (4-aminoethyl)benzenediazonium tetrafluoroborate salt was prepared as previously described.⁴⁶ All reactions in solution were routinely performed under an inert atmosphere of argon using conventional vacuum-line and glasswork techniques. The metal complexes were however handled in air in the solid state. Commercial grade NC3100 multi-walled carbon nanotubes (MWCNT) were obtained from Nanocyl (purity >95% in carbon) and used as received. Thermogravimetric (TGA) and XPS analysis of the MWNTs batch show the absence of amorphous carbon and the high purity of the MWCNTs with only 3.4% of inorganic materials analysed as SiO₂. No metallic impurities were detected by XPS. These data have been recently reported in reference 47. The gas diffusion layer (GDL) substrate was purchased from GORE Fuel Cell Technologies (CARBEL CL-P-02360).

Characterization methods and equipment are described in the Supplementary Information.

Preparation of GDL/MWCNT electrodes. In a typical experiment, a suspension of MWCNTs (2 mg) and Nafion® (200 µL of a 5% solution in alcohol/water) in ethanol (200 mL) was sonicated until

complete solubilisation (10 min). The MWCNT solution was deposited by slow filtration onto a GDL support (surface 10 cm²). The resulting material was air-dried for 10 min then heated for 30 min in an oven at 80°C. The estimated MWCNT charge is 0.2 mg·cm⁻².

Amine electro-functionalization of the GDL/MWCNT electrodes. The method is based on the previously reported literature procedure.¹⁸ The GDL/MWCNT material was employed as working electrode in an electrochemical cell, in the presence of (4-aminoethyl)benzenediazonium tetrafluoroborate (16 mg, 0.07 mmol) in a tetrabutylammonium tetrafluoroborate electrolyte solution (0.1 M) in acetonitrile (50 mL). Electrografting was performed through reduction of the diazonium salt by cyclic voltammetry recording 3 cycles at 20 mV·s⁻¹ between 0.0 V and -1.5 V vs Fc⁺⁰. The amine-functionalized electrode was washed 3 times by dipping in acetonitrile (10 min) and dried under a flow of nitrogen. A control sample was cut and used for measuring the blank signal.

Preparation of 2. To a solution of ligand **1** (197 mg, 0.70 mmol, see the supplementary information) in acetone (20 mL) was added a solution of CoCl₂·6H₂O (166 mg, 0.70 mmol) in acetone (10 mL). The mixture was stirred for 2 h under a continuous bubbling of air. The resulting green precipitate is filtered off, dissolved in CH₃CN, filtered and the solvent evaporated. The same operation was done with CH₂Cl₂ to finally yield a green powder (227 mg, 79% yield). ¹H NMR (300 MHz, acetone *d*⁶): δ ppm 19.40 (s, 1H, OH); 4.62–4.53 (m, 3H, CH₂, CHN₃); 3.88 (t, 13.2 Hz, 2H, CH₂); 2.77 (d, *J* = 1.7 Hz, 6H, CH₃); 2.55 (s, 6H, CH₃). ¹³C NMR (75 MHz, DMSO *d*⁶): δ ppm 176.9, 155.9, 58.6, 54.0, 18.2, 13.7. MS (ESI⁻): *m/z* 407.8 [M-H]⁻. Elemental analysis calcd. (%) for C₁₁H₁₈Cl₂CoN₇O₂·0.4 C₃H₆O: C 33.70, H 4.72, N 22.72; found: C 33.34, H 4.60, N 22.35.

Preparation of 3. A solution of **2** (200 mg, 0.48 mmol) and N-phthalimidyl-2-(cyclooct-2-yn-1-yloxy)acetate (165 mg, 1 equiv., see the supplementary information) in distilled CH₃CN (15 mL) was stirred at room temperature for 24 hours. After concentration under vacuum, the reaction mixture was purified on a Sephadex LH20 column (eluent: acetone / CH₂Cl₂, 1/1). The first fractions were evaporated and dried under vacuum to give a green powder (279 mg, 75 %). ¹H NMR (300 MHz, acetone *d*⁶): δ ppm 19.45 (s, 1H, OH), 7.98 (s, 4H, Ph), 5.80 – 5.52 (m, 1H, CH-O), 5.06 (ddd, *J* = 12.0, 7.7, 3.5 Hz, 1H, CH-N), 4.77 (dd, *J* = 27.3, 16.8 Hz, 2H, CH₂-N), 4.66 (s, 2H, CH₂-O), 4.75 – 4.39 (m, 2H, CH₂-N), 3.06 (dtd, *J* = 21.8, 14.9, 7.0 Hz, 2H, CH₂^{oct}), 2.68 (dd, *J* = 31.3, 1.2 Hz, 6H, CH₃), 2.59 (d, *J* = 11.8 Hz, 6H, CH₃), 2.30 – 2.19 (m, 1H, CH₂^{oct}), 1.99 – 1.91 (m, 1H, CH₂^{oct}), 1.87 – 1.13 (m, 6H, CH₂^{oct}). MS (ESI⁺): *m/z* 701.3 [M-Cl]. Elemental analysis calcd. (%) for C₂₉H₃₅Cl₂CoN₈O₇·0.5 CH₂Cl₂: C 45.85, H 4.62, N 14.26; found: C 46.08, H 5.01, N 13.89.

Covalent grafting of cobalt catalyst 3 on the amino electro-functionalized GDL/MWCNT electrode. The amine electro-functionalized GDL/MWCNT material was dipped in a 1 mM solution of cobalt catalyst **3** (3.5 mg) in distilled CH₂Cl₂ (5 mL) in the presence of 2,6-dimethylpyridine (5 μL, 8 equiv.) and agitated for 24h. The resulting cobalt-functionalized electrode was then removed from the solution, washed by dipping in CH₂Cl₂ then CH₃CN (10 min each), and dried under a flow of nitrogen.

For electrochemical studies, the functionalized electrode material was cut into several pieces and the active surface was delimited using solvent-resistant epoxy glue. The electrical contacts were made using conductive silver-based glue and a metallic wire. An identical procedure was used for preparing the control samples.

Figure captions

Figure 1. Synthetic methodology for the preparation of the CNT/Co material. The number of phenylene residues in the structure of the amino-decorated MWCNTs is arbitrary. X-ray structure of **2** (CCDC 896938, ORTEP diagram, 35% probability level displacement ellipsoids. Hydrogen atoms (except bridging H₂O) omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)-N(1) 1.8920(14), Co(1)-N(4) 1.8970(13), Co(1)-N(3) 1.9111(15), Co(1)-N(2) 1.9162(14), Co(1)-Cl(1) 2.2363(5), Co(1)-Cl(2) 2.2436(5), N(1)-Co(1)-N(4) 97.60(6), N(1)-Co(1)-N(3) 179.10(7), N(4)-Co(1)-N(3) 81.63(6), N(1)-Co(1)-N(2) 81.61(6), N(4)-Co(1)-N(2) 179.20(7), N(3)-Co(1)-N(2) 99.15(6), Cl(1)-Co(1)-Cl(2) 179.052(19), O(1)-H(20)-O(2) 169.29(15).

Figure 2. Electrochemical characterization. Cyclic voltammogram (black line) of **3** in acetonitrile (0.1 M *n*Bu₄NBF₄) recorded on a GDL/MWCNT electrode and the cyclic voltammogram (blue line) recorded on a GDL/MWCNT/Co functionalized electrode material in acetonitrile (0.1 M Et₄NCl), compared to the blank GDL/MWCNT electrode (dotted line) at 100 mV · s⁻¹. Integration of the electrochemical wave (patterned surface) allows the estimation of electroactive Co species on the functionalized electrode.

Figure 3. X-ray photoelectron spectroscopy (XPS) analysis. a) Survey) and b) Co_{2p} core level spectra of pristine MWCNTs (black), amino decorated MWCNTs (red) and CNT/Co material (blue) supported on fluorinated GDL substrate. The oxygen and fluorine present in the samples arise from defects (alcohol or carboxylic acid functions) on MWCNTs and from the fluorinated GDL membrane support, respectively. A careful analysis of the survey spectrum of pristine MWCNTs clearly shows the absence of metallic contaminants. The CNT/Co material was prepared in absence of Nafion to minimize the fluorine signal.

Figure 4. Electrocatalytic hydrogen evolution a) Linear sweep voltammetry (solid lines) recorded on a GDL/MWCNT/Co electrode (blue) compared to an unfunctionalized GDL/MWCNT electrode (black) in acetate buffer (0.1 M, pH 4.5) at low scan rates (0.1

$\text{mV}\cdot\text{s}^{-1}$) with simultaneous monitoring of H_2 evolution (dotted lines; N_2 was continuously bubbled through the electrolyte at a constant flow ($5 \text{ mL}\cdot\text{min}^{-1}$) during the experiment and the concentration of H_2 in the output gas was determined every 2 min by gas chromatography; faradaic yield is 100%). The use of an acetate buffer/ NaCl solution (0.1 M, pH 4.5) did not result in increased activity. *b*) Evolution of the current density during an electrolysis experiment run on a GDL/MWCNT/Co electrode (solid blue line) compared to a blank GDL/MWCNT electrode (black dotted line) at -0.59 V vs RHE in acetate buffer (0.1 M, pH 4.5). *c*) Charge passed during the same experiment (solid blue line) and the corresponding turnover numbers (solid red line) for electro-catalytic H_2 production.

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Author contributions

V. A., B. J., S. P. and M. F. designed research; E. S. A., P.-A. J., P. D. T., A. L., M. C.-K., M. M. and V. A. performed research; J. P. performed X-ray crystallographic studies; V. A. and E. S. A. wrote the paper.

Competing financial interests

Patent applications (EP-08 290 988.8 and E.N.10 53019) have been filed for the preparation of azide-appended diimine-dioxime complexes such as **2** and their grafting onto electrode materials.

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