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COMMUNICATION

Versatile functionalization of carbon electrodes with a polypyridine ligand: metallation and electrocatalytic H⁺ and CO₂ reductionNoémie Elgrishi,^a Sophie Griveau,^{b,c,d,e} Matthew B. Chambers,^a Fethi Bedioui^{b,c,d,e} and Marc Fontecave^{*a}

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A strategy is proposed for immobilization of homogeneous catalysts whereby a glassy carbon electrode is functionalized by electro-grafting of a ligand, terpyridine. The modified electrode can easily be metallated with cobalt and shows activity towards catalytic proton and CO₂ reduction. The metal can be removed and the electrode re-metallated at will.

Heterogeneous catalysis is often favored industrially due to more facile product isolation and catalyst regeneration and recovery.^{1,2,3} However, mechanistic studies of catalytic processes are more common for homogeneous systems as molecular compounds afford the opportunity to more easily design and tune the coordination environment of the catalyst and due to the availability of common solution phase *in situ* spectroscopic techniques.^{4,5,6,7,8,9} To reconcile these two approaches, homogeneous catalysts are often immobilized on heterogeneous supports.^{10,11,12,13,14,15,16,17} In a case wherein the solid support is a conductive surface, this strategy provides access to modified electrodes with the activity of the particular grafted molecule. Such procedures have been implemented for a wide variety of catalysts using a range of specific techniques, from electro-polymerization of phenanthroline¹⁸ or vinyl^{19,20} or pyrrole^{21,22} functional groups, to phosphonates^{23,24} or thiols groups²⁵, pi-stacking interactions between a pyrene motif and a carbon electrode^{26,27} or diazotization²⁸ to name a few. While successful, one common limitation of these techniques is that the entire catalytic entity must be synthesized prior to immobilization. Therefore, beyond this primary synthetic effort, the scope of activity for each modified electrode is restricted to only the specific reactivity of each molecular motif.

Here a new perspective of this strategy was investigated: grafting a versatile ligand first, followed by reversible metal incorporation required for catalysis. This presents the advantage of potentially being able to functionalize the electrode with a wide range of different metals for different purposes. The immobilizing strategy that has been chosen herein is ligand diazotization followed by controlled electro-grafting onto a glassy carbon electrode, which has been successfully implemented in the grafting of a wide range of compounds.^{29,30,31,32,33,34,35,36}

The terpyridine (tpy) motif is present in numerous catalysts for the reduction of H⁺, CO₂, O₂, NAD⁺ just to name a few of interest to the energy landscape, not to mention water oxidation.^{37,38,39,40,41,42,43,44,45} We have previously studied tpy

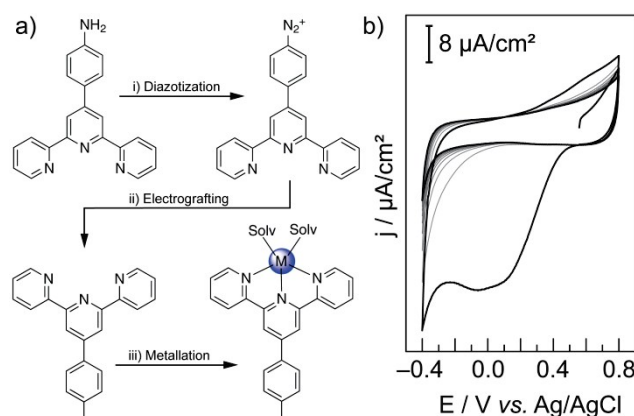


Fig. 1 a) Simplified synthetic scheme for the preparation of the modified electrodes in 3 steps: i) NOBF₄, MeCN/Sulfolane (1:1), -40°C, 40 min, Ar, shielded from light. ii) Cyclic voltammetry, MeCN, TBAPF₆ 0.1M, Ar, shielded from light, 10 cycles from +0.8 to -0.4 V vs. Ag/AgCl, 50 mV/s, glassy carbon electrode. iii) Soaking in a DMF solution of 75 mM CoCl₂. b) Cyclic voltammograms of the electrografting procedure: 50 mV/s in MeCN, 10 scans. The first and last scans are in black, cycles 2-9 are in grey for clarity.

motifs on first row transition metals for their ability to reduce CO₂ to CO in DMF solutions as well as H⁺ to H₂ and numerous hints pointed to the active catalyst comprising of only one tpy ligand per cobalt atom.^{46,47} We thus sought out to functionalize a glassy carbon electrode by electro-grafting of a diazotized version of the tpy ligand, and subsequent metallation to study its catalytic activity towards proton and CO₂ reduction.

To this end a terpyridine based ligand, tpy-Ph-NH₂ (Fig. 1a, top left), was diazotized by reacting with NOBF₄ in a MeCN/sulfolane (1:1) solution at -30 °C for 40 min.⁴⁸ The dark red powder of tpy-Ph-N₂⁺ BF₄⁻ was dissolved in MeCN with 0.1M of tetrabutylammonium hexafluorophosphate (TBAPF₆), shielded from light and the solution degassed with argon. A bare polished glassy carbon electrode was immersed in the solution and electro-grafting was achieved by cycling the potential from +0.80 V to -0.40 V, at 50 mV/s until the cyclic voltammograms were super-imposable (10 scans). In this potential window, a reduction event occurs starting at +0.50 V vs. Ag/AgCl, corresponding to the reduction of the diazonium group. This liberates N₂ and generates a radical that is believed to react with the glassy carbon electrode, yielding a modified surface. The resulting organic layer was shown to be insulating in the potential

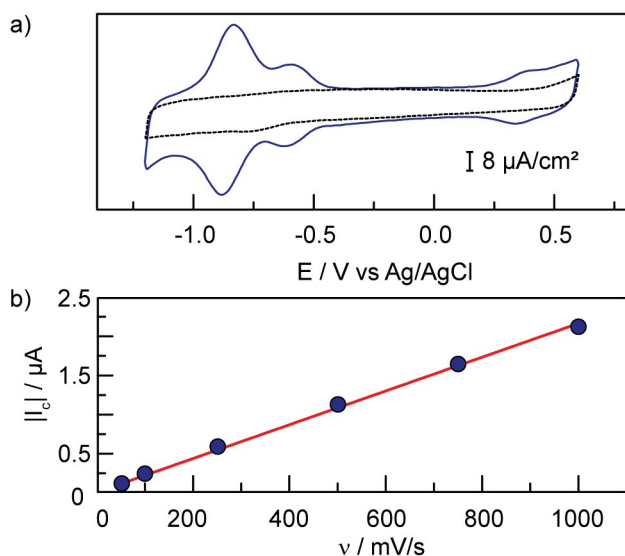


Fig. 2 a) Cyclic voltammograms in DMF solutions containing 0.1 M of TBAPF₆ as supporting electrolyte, under Ar, at 100 mV/s of a bare glassy carbon electrode (---black dashed line) and the grafted electrode metallated with cobalt (—blue line). b) Absolute value of the cathodic current observed on the peak at -0.86 V and its linear evolution with scan rate (correlation coefficient: 0.999).

window scanned, and thus the grafting process ended as the electrode was completely covered (Fig. 1b).

The grafted electrode was rinsed and characterized by cyclic voltammetry in DMF with TBAPF₆ as supporting electrolyte (0.1 M). The electrode presented no signal in the potential window interrogated (+0.60; -1.50 V) under argon and was virtually indistinguishable from a bare electrode under these conditions (ESI Fig. S1). A grafted layer was however present, as evidenced by the silencing of the redox signal of the probe ferrocyanide compared to the signal observed on the bare electrode (ESI Fig. S2).

The electrode thusly modified was immersed in a solution of CoCl₂ 75 mM in DMF for 3h at room temperature and subsequently thoroughly rinsed in DMF and H₂O for 15 minutes. The electrode was then characterized by cyclic voltammetry, and exhibited several redox events in the window scanned, none of which were present in the ligand modified electrode (Fig. 2a). The minor features at -0.61 and $+0.37$ V are attributed to a Co(tpy)₂^{II/I} and ^{III/II} respectively by comparison to the features observed in a Co(tpy)₂ homogeneous solution, and are believed to be a consequence of the significant roughness of the electrode allowing two adjacent terpyridine ligands to bind one cobalt ion.⁴⁶ The major feature at -0.86 V is attributed to a cobalt complex containing only one terpyridine ligand, again by analogy with the homogenous system.⁴⁷ This claim is further supported by the observation of a pre-feature during the first scan of a modified electrode metallated with CoCl₂ when rinsed with DMF and not water (ESI Fig. S3). This pre-feature is consistent with the liberation of the chloride ions in solution, and replacement with solvent molecules.^{20,27}

The electrochemical features are due to surface-bound species, as evidenced by the fact that i) they are observed in a pristine electrolyte solution with the modified electrode, ii) their intensity varies linearly with the scan rate applied (Fig. 2b). The area of the peaks observed in the cyclic voltammograms allow for easy

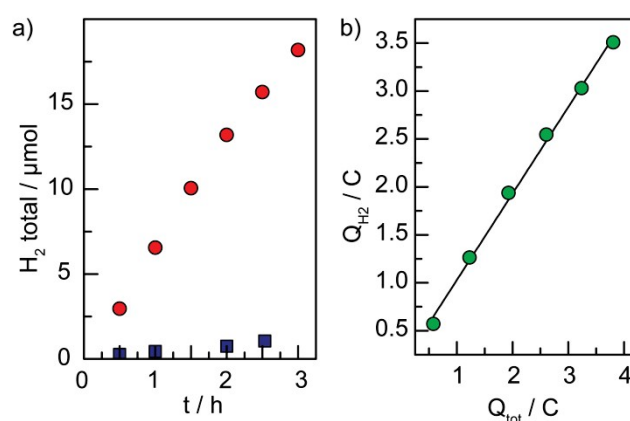


Fig. 3 a) Total amount of H₂ produced during a bulk electrolysis at -1.50 V of a modified (● red circles) and bare (■ blue squares) glassy carbon electrode from a DMF solution with 0.1M TBAPF₆ as supporting electrolyte and 0.1 M acetic acid as proton source. b) Total charge accounted for by the H₂ produced vs. total charge passed in the bulk electrolysis of the modified electrode (● green circles). The correlation coefficient is 0.996, and the faradic yield for H₂ production, given by the slope of the line, is $90\% \pm 5\%$.

estimation of the density of cobalt atoms on the surface. An estimated surface coverage of $5 \cdot 10^{-10}$ mol/cm² was obtained, corresponding to close to a monolayer. This shows the advantage of this grafting method, since an equivalent monolayer of cobalt complex is easily obtained.

Once functionalized with the ligand tpy and metallated, the cobalt can easily be removed to recover the modified electrode by soaking in a 50 mM solution of ethylenediaminetetraacetic acid (EDTA) in water at pH 10. After 3 hours in the EDTA solution, the pristine modified electrode is recovered (ESI Fig. S4), and can be re-metallated at will. In order to quantify the quality of the recovered modified electrode, cobalt was re-introduced, and the peaks attributed to cobalt complexes showed that over 95% of the intensity of the original features were recovered, which demonstrates that the grafted layer of tpy ligand was not irreversibly modified by the de-metallation procedure (ESI Fig. S4). Thanks to this simple and ready to use functionalized electrode, different metal salts can be tried, and their catalytic activity assayed easily. A tpy-modified electrode was metallated with nickel as a proof of concept, and the features of the nickel-metallated tpy-modified electrode are similar to those observed in solution (ESI Fig. S5).

Having obtained the modified electrodes, we next assayed the derivatives with cobalt for their catalytic properties for the reduction of protons and CO₂. When 4.3 mM of acetic acid was added to a DMF solution containing 0.1 M TBAPF₆ as supporting electrolyte, a strong cathodic current increase was observed starting at -1.06 V vs. Ag/AgCl, with an 11-fold increase in intensity at -1.40 V vs. Ag/AgCl compared to the behavior observed in the absence of acid, or in the presence of acid with a bare polished glassy carbon electrode. This suggests catalytic proton reduction by the modified electrode (ESI Fig. S6).

To confirm the identity of the catalytic process, a 1.4 cm diameter glassy carbon electrode was grafted with the ligand, metallated, and tested in DMF/TBAPF₆ under Ar with added 0.1 M acetic acid in a bulk electrolysis at -1.50 V vs. Ag/AgCl. A current density of 300 μ A/cm² was observed and was sustained

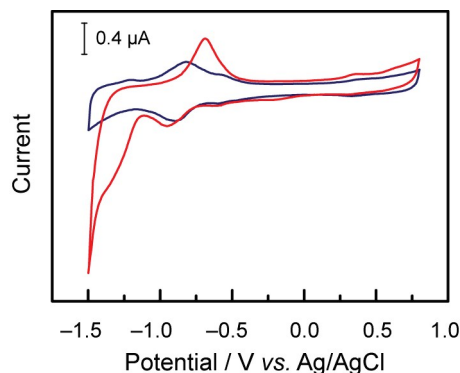


Fig. 4 Cyclic voltammograms in DMF, TBAPF₆ 0.1M, of a glassy carbon electrode modified with the tpy ligand freshly metallated with CoCl₂ under Ar (—blue) and CO₂ (—red) at 100 mV/s.

during the 3 hours that the experiment lasted (ESI Fig. S7), during which time a steady production of H₂ was observed (Fig. 3a). The presence of H₂ was confirmed by GC measurements. This production of H₂ represented 6 μmol/h for the 1.4 cm diameter electrode corresponding to an apparent turnover number (TON) of 24 000 when the electrolysis was stopped (3h). Of note, the activity was still sustained at the end of the experiment and by no mean is this TON implied to be a maximum. The turnover frequency (TOF) obtained from this experiment was 2.2 s⁻¹. The faradic yield for H₂ production obtained during the bulk electrolysis as given in Fig. 3b is ≥ 90%, confirming H₂ production as the main reduction event.

One of the advantages of immobilizing homogeneous catalysts onto the surface of electrodes is the possibility to diversify the nature of the solvents that can be used, including water. To test the possibility of utilizing a Co-tpy modified electrode as a catalyst for H⁺ reduction from neutral water, a grafted and metallated electrode was immersed in a phosphate buffer at pH 7 in water under argon. As the electrode was scanned to negative potentials, an 18-fold increase in cathodic current was observed at -1.50 V compared to a bare glassy carbon electrode (ESI Fig. S8). To reach the same current intensities on a bare glassy carbon electrode, a potential about 370 mV more negative has to be applied, confirming the activity of the electrodes modified with Co-tpy as catalysts for the reduction of protons in phosphate buffer.

The modified electrodes were also assayed for activity towards CO₂ reduction in DMF solutions containing 0.1 M TBAPF₆ as supporting electrolyte. A strong cathodic current enhancement was observed under CO₂ compared to argon as is observed for the corresponding homogeneous catalysts, with an onset at -1.12 V vs. Ag/AgCl (Fig. 4).^{46,47} However, an anodic feature was also observed under CO₂ at -0.69 V vs. Ag/AgCl. This feature was not observed either in homogeneous solutions of Co-tpy or on a bare electrode, and is tentatively assigned to the formation of a Co—CO adduct as supported by the electrochemical feature observed in CVs recorded under an atmosphere of CO (ESI Fig. S9). Bulk electrolysis at -1.50 V vs. Ag/AgCl in DMF under CO₂ of a 1.4 cm diameter tpy-modified electrode metallated with cobalt exhibited a rapid decrease of current during the first 30 minutes to reach baseline levels. During those 30 minutes, 55 nmol of CO were produced, corresponding to a TON of 70 per cobalt atom on the electrode (ESI Fig. S10).

In summary, we have reported on the simple preparation of glassy carbon electrode functionalized with terpyridine, a common stable and cheap polypyridyl ligand with broad applications. This strategy allows a versatility of the end uses of such modified electrodes through reversible metallation with a variety of metal ions, here non-noble cobalt and nickel ions, to obtain immobilized catalysts. Specifically, we show that the cobalt-modified electrode displays excellent stability and electrocatalytic performances during proton reduction into hydrogen, in both organic and aqueous solvents. Despite the modest activity for CO₂ reduction and limited stability, it is comparable to that which has been recently reported for rhenium-modified electrodes²⁷. However, our electrode is one of the very rare examples of glassy carbon electrodes functionalized with non-noble catalysts for CO₂ reduction⁴⁹ and provides an interesting basis for future optimization.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: Experimental procedure as well as supplementary figures as described in the text. See DOI: 10.1039/b000000x/.
- ‡ Diazonium electrografting can lead to branched ligands, which could also result in a configuration where two terpyridine ligand can coordinate the same cobalt ion, see ref 36.
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