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COMMUNICATION

Facile Heterogenization of a Cobalt Catalyst via Graphene Adsorption: Robust and Versatile Dihydrogen Production Systems

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A heterogeneous dihydrogen (H₂) production system has been attained by simply soaking electrodes made from electro-deposited graphene on FTO plated glass in solutions of a cobalt bis(dithiolate) compound. The resulting electrodes are active in weakly acidic aqueous solutions (pH > 3), have relatively low overpotentials (0.37 V versus platinum), show high catalytic rates (TOF > 1000 s⁻¹), and are resistant to degradation by dioxygen.

In the search for an economically viable solution for carbon-neutral dihydrogen (H₂) generation, the pool of low-cost early transition metal dihydrogen production catalysts, particularly hydrogenase models, has been fished extensively. A colourful array of iron, nickel and cobalt catalysts (among others) has been crafted, many of which show outstanding turnover frequencies and catalytic lifetimes.^[1] Yet many catalytic systems are still being designed with synthetically challenging and hence, costly ligand manifolds, and homogeneous components, which are both unsuitable for implementation at scale. An ideal system would require minimal synthetic effort, only inexpensive materials, and have the capability to be directly tied to a renewable energy source to produce clean H₂ without further modification. To achieve such a heterogeneous catalyst, adsorption to graphene provides an incredibly versatile option open to nearly all aromatic systems, as shown for graphitic systems in many examples.^[2] Additionally, graphene itself serves as a means to access a number of different electrode materials, as its electro-deposition on many substrates has been demonstrated.^[3] For implementation into (photo)cathode systems and eventual coupling to water oxidation half-cells, such a pliable catalyst interface is invaluable.

In this paper we report a facile means of designing a graphene-interfaced heterogeneous catalyst system using widely available, inexpensive materials. The catalyst, graphene surfaces, and method of combination reported here require minimal synthetic effort and time to prepare. Resulting catalyst-adsorbed graphene surfaces indicate activity for H₂ formation at reasonable overpotentials in weakly acidic aqueous media. Most enticingly, this system shows resilience to O₂ exposure and resistance to catalyst leaching.

Graphene oxide was prepared from flake graphite via Hummer's method^[4], and an aqueous suspension was prepared in a weakly alkaline carbonate-buffered system. Graphene-coated

substrates were accessible by cyclic voltammetry (CV) in the graphene oxide suspension, using the substrate (here: metal oxide-coated glass) as the working electrode (**Figure S3**). For ease of study, initial testing was performed on glass coated fluorine-doped tin oxide (FTO) electrodes, which provide a very generous cathodic window (~1.3 vs. SCE) at very low cost.^[5] To afford the catalyst-adsorbed surfaces, the graphene-coated FTO surfaces were soaked in a 5 mM solution of catalyst in acetonitrile for 12 hours. Keeping simplicity in design, the H₂ production catalyst selected for use here is a simple cobalt bis(dithiolate) complex that is afforded in high yield from a one-pot reaction with inexpensive materials (Chart 1).^[6]

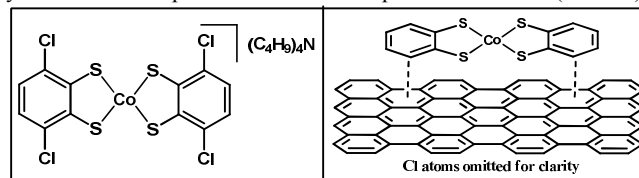


Chart 1. Co bis(dithiolate) compound (**1**) used for graphene adsorption, (left), schematic representation of π -stacking interactions (right).

This compound has been shown by McNamara et al. to display impressive activity (TOF = 1,400 h⁻¹) and exemplary stability (TON = 6000) at low overpotentials for both electro- and photocatalytic (using Ru-bpy) dihydrogen generation in homogeneous phase.^[6] It is notable that no synthetic manipulation is required for graphene adsorption of this compound, which is ideal for applications at scale, in comparison with other catalyst designs which often require custom introduction of aromatic moieties for surface attachment (via involved synthetic pathways).^[2b]

CV analysis of catalyst-soaked FTO/graphene surfaces (after extensive rinsing and sonication regimens) in aqueous solutions indicates that the compound is bound, showing quasi-reversible redox couples at an average potential of -0.49 V. It is noteworthy that the redox couple of **1** is roughly similar to that observed in solution (**Figure 1**).^[6] Importantly, upon addition of trifluoroacetic acid (TFA, pK_a = 0.23), CVs of the FTO/graphene/**1** system show a sharp increase in current during cathodic scanning at -0.73 V, a behaviour indicative of electrocatalytic reduction of protons from TFA (**Figure 2**). This activity is observed with an overpotential of only 0.37 V as compared to the reduction of TFA at a platinum electrode under the same conditions (**Figure S6**). Testing of the

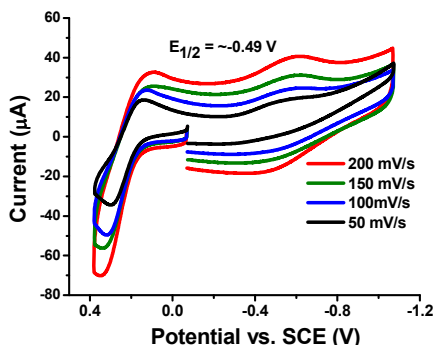


Figure 1. $\text{Co}^{\text{III/II}}$ couple observed for FTO/graphene/1 in 0.1 M KPF_6 aqueous solution. The working electrode is catalyst-adsorbed graphene on FTO, the auxiliary electrode is a platinum wire, and the reference is Ag/AgCl (sat. KCl).

same graphene electrode in identical conditions prior to catalyst adsorption showed minimal background current, confirming this activity as being directly a result of the catalyst's presence. The half-wave potential ($E_{\text{cat}} = -0.85$ V) and catalytic peak potential ($i_{\text{pc}} = -1.0$ V) are both nearly identical to those reported in homogeneous phase, suggesting the catalyst is unaltered upon adsorption to graphene.^[6]

Analysis of activity upon increasing TFA addition shows a linear correlation (under CV conditions; **Figure S5**) with no activity saturation observed at the acid concentrations used. Replacing the acidic solution after electrochemical analysis with a new electrolyte-only solution (pH = 7.5) shows the same redox couple seen in the first solution. Addition of TFA to the second solution shows the same activity as observed in the preceding run, and repetition of this process shows no significant decrease of catalyst activity (**Figure S7**). These results indicate the catalyst-adsorbed surfaces are O_2 stable and resistant to leaching under the experimental conditions (all manipulations done in air). XPS analysis of graphene/1 surfaces after electrochemical testing confirms these findings (**Figure S1**). To assure these responses are not specific to just TFA, electrochemical analyses of the catalyst-adsorbed graphene surfaces with dilute hydrochloric acid solutions were also performed. These tests elicit identical responses in electrocatalytic behaviour (**Figure S8**).

The proton reduction mechanism of **1** on the graphene surface appears to correspond to that reported in solution by McNamara and coworkers. Upon addition of acid, no significant change is seen in the reduction event at approximately -0.5 V, however a new wave appears at a potential roughly 0.25 V more cathodic than the original wave (**Figure S9**). This is indicative of an initial reduction of the cobalt anion to the dianion preceding rapid protonation of the dianion. This protonation event allows for a

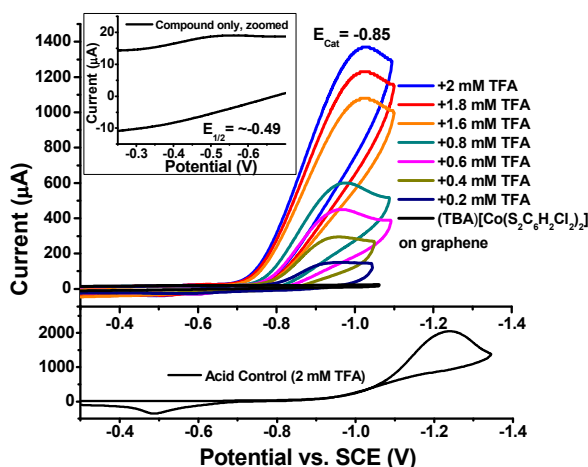


Figure 2. FTO/graphene/1 working electrode with the addition of trifluoroacetic acid. Counter electrode is a platinum wire and the reference is Ag/AgCl (sat. KCl).

subsequent reduction unobserved in the absence of acid. While the final protonation event was not observed directly, these data suggest either an ECEC or ECCE type mechanism. These results show that the activity profile for **1** on graphene closely mirrors that reported for **1** in homogeneous solution. These findings are indicative of the direct adsorption of **1** on the graphene surface and indicate a mechanism analogous to the homogeneous catalyst.

The bare FTO, FTO/graphene, and FTO/graphene/1 surfaces were analyzed by X-ray photoelectron spectroscopy (XPS). The high-resolution C 1s XPS data (**Figure 3a**) of a bare FTO surface exhibit only features consistent with adventitious carbon.^[7] After graphene deposition, signatures indicative of C-O (hydroxyl, epoxy) groups at 286.7 eV and C=O (carbonyl groups) at 288.4 eV are prominent. These signatures are consistent with previous reports of reduced graphene oxide on surfaces.^[8] After soaking the graphene surface in catalyst, a peak at 287.7 eV emerges in the C 1s spectra, corresponding to a C-S bonding energy which would be expected for **1** (originating from the dithiolate ligand). This is corroborated by the high-resolution Co 2p and S 2p spectra (**Figure 3b, c**) where features of Co and S are clearly present after exposure to catalyst. A feature corresponding to the Co-S energy is also present in the Co 2p data;

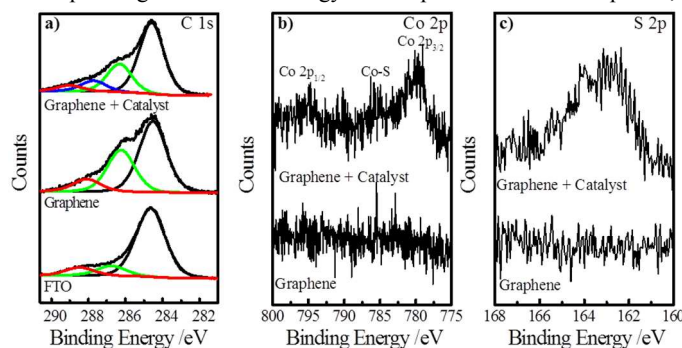


Figure 3. (a) High-resolution C 1s XPS data of (bottom) bare FTO, (middle) FTO/graphene, and (top) FTO/graphene surfaces after soaking in a 5 mM solution of **1** in acetonitrile for 12 hours. Co 2p (b) and S 2p (c) XPS data of (bottom) graphene-deposited FTO glass and (top) the graphene surfaces after deposition of **1** (using similar conditions). However it is difficult to distinguish above the background.

To confirm the facile heterogenization of compound **1** on a more controlled surface, adsorption on a highly-ordered pyrolytic graphite electrode (HOPG, Pine Instrument Co.) was also studied under the same conditions. For the purpose of these studies, the highly-ordered nature of the graphite surface was intended to simulate a sheet of graphene in terms of electrostatic interactions. Here, compound **1** is seen to exhibit a quasi-reversible redox couple at approximately -0.76 V (**Figure S10**). Addition of TFA to graphite/1 shows catalytic current at an onset potential slightly more cathodic than the observed redox couple, approximately -0.77 V (**Figure 4**). This current is absent at the same HOPG electrode prior to soaking in catalyst, and is indicative of dihydrogen production from TFA, with a peak catalytic potential of -1 V and a current half-maximum potential of -0.92 V.

Increasing acid concentrations lead to a linear increase in catalytic current (under CV conditions), with no activity saturation observed at the acid concentrations studied (**Figure S11**). Excitingly, analysis of **1** on graphite at higher TFA concentrations (>20 mM) showed such high levels of dihydrogen production that peak catalytic currents were perturbed by gas bubbles at the graphite electrode, still without reaching activity-limited currents (**Figure S14**).

The similarity between the catalytic onset potential of **1** and its redox couple in the absence of acid on graphite suggests that reduction precedes protonation, possibly indicating an ECEC- or ECCE-type mechanism (**Figure S13**). It is therefore interesting to

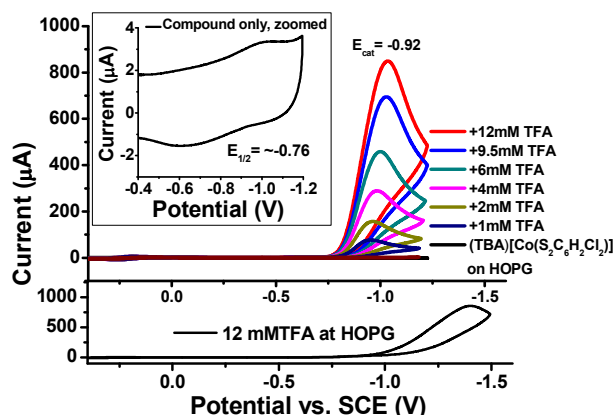


Figure 4. Compound **1** adsorbed on HOPG (working electrode) with the addition of TFA. A platinum wire is used as counter electrode and Ag/AgCl (sat. KCl) as reference.

note that the overall mechanism is similar in the FTO/graphene/**1** and graphite/**1** systems, but that in the former case a ~ 0.2 V cathodic shift of the catalytic relative to the first redox wave is observed. This may indicate an inherent difference in the compound adsorption/interaction with graphene compared to graphite.

The turnover frequency (TOF) of the immobilized catalyst systems for dihydrogen production can be estimated using direct comparison of cathodic peaks in the presence and absence of acid (eqn 1, SI). This method yields conservative estimates of 1007 s^{-1} and 701 s^{-1} for the graphene/**1** system in TFA and HCl, respectively. It is noteworthy that these rates dramatically exceed those reported for the compound in homogeneous solution ($1,400 \text{ h}^{-1}$). One problem for the graphene/**1** system at high acid concentrations is background acid reduction as well as tin oxide reduction at the exposed FTO electrode surfaces (see acid controls, Figures 2 and S8). Hence, acid-saturation conditions could not be reached. Using the same method to calculate TOF for graphite/**1** systems gives a rate of $6,182 \text{ s}^{-1}$. It is noteworthy that this level of activity is comparable to that of the renowned nickel bis(diphosphine) catalysts (although at a comparably higher overpotential), and is among the highest activities reported for cobalt-based hydrogen production systems.^[9] This rate was again determined in conditions where the catalyst activity was not saturated, this time due to disturbance of the voltammograms by H_2 production and background proton reduction by graphite at high acid concentrations (Figure S14). Therefore, catalytic rates for heterogeneous systems of **1** were also analysed by the 'foot of the catalytic wave' method (eqn (2) & (3), SI). This method provides estimates of $5.77 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $3.35 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the graphene/**1** systems in HCl and TFA, respectively, and $3.68 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for the graphite/**1** system with TFA. While these estimates are exceptionally high (as expected since this method is less reliable in instances of substrate diffusion-limited activity), in combination with the results from eqn (1) this demonstrates that heterogeneous

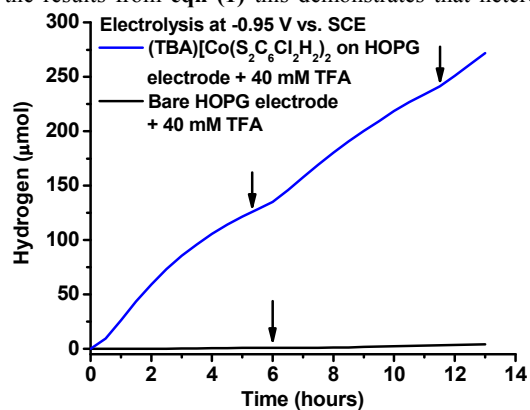


Figure 5. Electrolysis of compound **1** adsorbed on graphite in 40 mM TFA solution at -0.95 vs. SCE. Arrows indicate addition of supplemental acid (40 mM aliquots).

systems of **1** immobilized on graphitic surfaces have impressive dihydrogen production activities.

Electrolysis studies of **1** directly adsorbed on graphite were performed to assess our heterogeneous system under multiple turnover conditions, with dihydrogen production monitored by gas chromatography (Figure 5). After 12 hours of a -0.95 V applied potential in a 12 mM TFA solution, the graphite/**1** system had produced over $250 \mu\text{mol}$ of hydrogen and activity was still not seen to subside. The current observed correlated closely with the evolved hydrogen (Figure S16) and a faradaic efficiency close to 100% was determined, indicating the exclusive use of injected electrons for proton reduction. An initial rate of $2.88 \times 10^{16} [\text{molecules } \text{H}_2] \text{ s}^{-1}$ for H_2 production was calculated for a graphite/**1** electrode of 0.2 cm^2 surface area. Unfortunately, the attempt to calculate a molecular TOF was prevented due to difficulty in accurately quantifying the amount of **1** on the graphite surface. Future work to determine the molecular TOF and long-term electrolysis studies are underway.

In summary, our initial studies show that heterogeneous cobalt bis(dithiolate) electrocatalysts are easily afforded without the need of time consuming and costly functionalization of the ligand framework with large aromatic groups. These systems display total catalysis in practically relevant pH ranges ($\text{pH} > 3$), and no substantial degradation or leaching is evident from either acidic conditions or O_2 exposure in the experiments conducted. With the wide range of substrates available for graphene deposition, this technique ensures that heterogeneous dihydrogen-generation catalysis is viable on a variety of materials, giving nearly limitless possibility for materials engineering. Applications in semiconductor systems are of particular interest, and corresponding studies are underway.

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Notes and references

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Electronic Supplementary Information (ESI) available: experimental details and additional electrochemical data. See DOI: 10.1039/c000000x/

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TOC Figure

