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The modification of glassy carbon and gold electrodes with aryl diazonium salt: The impact of the electrode materials on the rate of heterogeneous electron transfer

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Abstract

The heterogeneous electron-transfer properties of ferrocenemethylamine coupled to a series of mixed 4-carboxyphenyl/phenyl monolayers on glassy carbon (GC) and gold electrodes were investigated, by cyclic voltammetry, in aqueous buffer solutions. The electrodes were derivatized in a step-wise process. Electrochemical reduction of mixtures of 4-carboxyphenyl and phenyl diazonium salts on the electrode surfaces yielded stable monolayers. The introduction of carboxylic acid moieties onto the surfaces was verified by X-ray photoelectron spectroscopy. Subsequently the 4-carboxyphenyl moieties were activated using water-soluble carbodiimide and *N*-hydroxysuccinimide and reacted with ferrocenemethylamine. The rate constants of electron transfer through the monolayer systems were determined from cyclic voltammograms using the Marcus theory for electron transfer and were found to be an order of magnitude higher for the ferrocene-modified monolayer systems on gold than those on GC electrodes. The results suggest the electrode material has an important influence on the rate of electron transfer.

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Keywords: Self-assembled monolayers; Electron transfer; Carbon; Gold; Diazonium salts

1. Introduction

The modification of conducting surfaces with monolayers has received extensive research interest of late because of their utility as model systems for understanding electron transfer [1,2], molecular electronics [3,4], bioelectronics [5,6] and sensors [7] amongst other applications. The most popular chemistry for forming monolayers on electrode surfaces is alkanethiol self-assembly onto coinage metals, in particular gold [8], although other systems have also attracted interest such as silanes on metal oxide electrodes [9] and alkenes on highly doped silicon [10]. The attractiveness of gold–

thiol chemistry is that well ordered monolayers can be formed relatively easily, with a reasonably strong bond formed between the organic molecule and the electrode, and that a diverse range of molecules can be synthesized with which to modify an electrode. The advantages of gold–thiol chemistry are somewhat offset by a number of disadvantages, including alkanethiols being oxidatively or reductively desorbed at potentials typically outside the window defined by -800 to $+800$ mV versus Ag/AgCl. Other disadvantages include: alkanethiols being desorbed at temperatures over 100 °C, gold being a highly mobile surface which results in the monolayers moving across the electrode surface, the gold–thiolate bond being prone to oxidation and the gold/thiol junction creating a rather large tunneling barrier (~ 2 eV) [11]. The last point regarding a large tunneling barrier

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has implications for the rate of electron transfer from the organic monolayer to the electrode which is important for all molecular scale devices where communication with the macroscopic world is achieved through electron transport.

We are interested in alternative monolayer systems to gold–thiol chemistry which overcome some of the disadvantages but do not severely compromise the advantages of gold/thiol chemistry. The electrochemical reduction of aryl diazonium salts is one possible alternative which has most frequently been used as a method for the covalent derivatization of glassy carbon (GC) surfaces [12–14]. The reduction reaction results in the loss of the N_2 and the formation of a carbon–carbon covalent bond which is strong, stable over both time and temperature, non-polar and conjugated [11]. Thus, the conjugated carbon network in the GC electrode can be thought of as continuing into the monolayer system rather than the abrupt change from electrons being in a metallic environment to an organic environment. The continuity of the electrode material into the monolayer has resulted in the suggestion that GC electrodes modified by aryl diazonium salts have the potential to reduce the barrier towards electron transfer from the carbon electrode into the monolayer [11]. McCreery and coworkers [15–18] have extensively studied the electron transfer kinetics of GC surfaces in different redox probe solutions. However, to the best of our knowledge heterogeneous electron transfer between redox active molecules and GC electrodes through aryl diazonium salt derived monolayers has yet to be investigated. Nor has the notion that the C–C bond will allow efficient electron transfer.

The attractiveness of aryl diazonium salts are enhanced further by recent studies showing they can also be grafted to a variety of metal [19,20] and semiconductor [21] surfaces as well as carbon nanotubes [22]. This feature raises the exciting possibility of one monolayer forming system being suitable for a large range of electrode materials for a diverse range of applications. This possibility is helped by a rich array of different diazonium salts which have now been prepared including molecular wires [23] and polyethylene glycol terminated molecules designed to resist protein adsorption [24,25]. The purpose of this study is to modify GC and gold substrates using mixtures of aryl diazonium salt molecules (introducing phenyl and 4-carboxyphenyl groups onto the surface) and to compare the kinetics of electron transfer to GC and gold surfaces from the same ferrocene-based monolayer system. A similar ferrocene-based system prepared by a mixed self-assembled monolayers (SAMs) of 4-mercaptobenzoic acid (MBA) and 1-propanethiol (PT) has also been prepared on gold surfaces and the rates of electron transfer have been studied for further comparison.

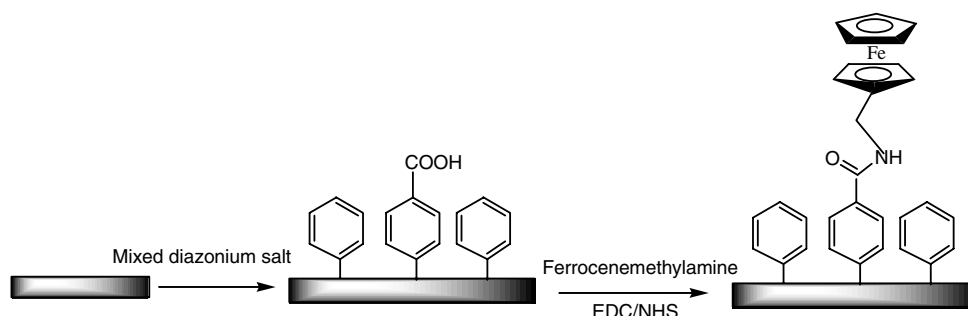
2. Experimental

2.1. Reagents and materials

Tetrabutylammonium tetrafluoroborate (NBu_4BF_4), sodium tetrafluoroborate ($NaBF_4$), *p*-aminobenzoic acid, aniline, 4-mercaptobenzoic acid (MBA), 1-propanethiol (PT), ferricyanide ($K_4Fe(CN)_6$), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS), *N*-[2-hydroxyethyl]piperazine-*N'*-[2-ethanesulfonic acid] (HEPES), ferrocenecarboxaldehyde, sodium cyanoborohydride and acetonitrile (CH_3CN , HPLC grade) were obtained from Sigma (Sydney, Australia). Benzoic acid diazonium tetrafluoroborate and benzene diazonium tetrafluoroborate were synthesized according to the method by Saby et al. [26]. Ferrocenemethylamine was synthesized using the procedure from Kraatz [27]. Reagent grade dipotassium orthophosphate, potassium dihydrogen orthophosphate, potassium chloride, sodium hydroxide, sodium chloride, sodium nitrite, ammonium acetate, sulphuric acid, hydrochloric acid, methanol and diethyl ether were purchased from Ajax Chemicals Pty. Ltd. (Sydney, Australia). All reagents were used as received, and aqueous solutions were prepared with purified water ($18\text{ M}\Omega\text{ cm}^{-1}$, Millipore, Sydney, Australia). Phosphate buffer solutions used in this work contained 0.05 M KCl and 0.05 M K_2HPO_4/KH_2PO_4 and were adjusted with NaOH or HCl solution.

2.2. Modification of electrodes

The GC and gold electrodes were modified with diazonium salts followed by attachment of ferrocenemethylamine as depicted in Scheme 1. The GC electrodes were purchased commercially (Bioanalytical System Inc., USA) as 3-mm-diameter rods. The electrodes were polished successively in 1.0, 0.3, and 0.05 μm alumina slurries made from dry Buehler alumina and Milli-Q water on microcloth pads (Buehler, Lake Bluff, IL, USA). The electrodes were thoroughly rinsed with Milli-Q water and sonicated in Milli-Q water for 5 min between polishing steps. Before derivatization, the electrodes were dried with an argon gas stream. The bare GC electrodes had an electrochemical roughness factor (the ratio of the electrochemical area to geometric area) of 1.43. Surface derivatization of GC electrodes was performed in a solution of 1 mM aryl diazonium salt and 0.1 M $NaBu_4BF_4$ in acetonitrile using cyclic voltammetry (CV) with a scan rate of 100 mV s^{-1} for two cycles between +1.0 and –1.0 V. The diazonium salt solution was deaerated with argon for at least 15 min prior to derivatization. The electrodes were rinsed with copious amounts of acetonitrile and then water and dried under a stream of argon prior to the next step.



Scheme 1. Schematic of ferrocenemethylamine immobilized covalently on mixed monolayers of 4-carboxyphenyl and phenyl moieties.

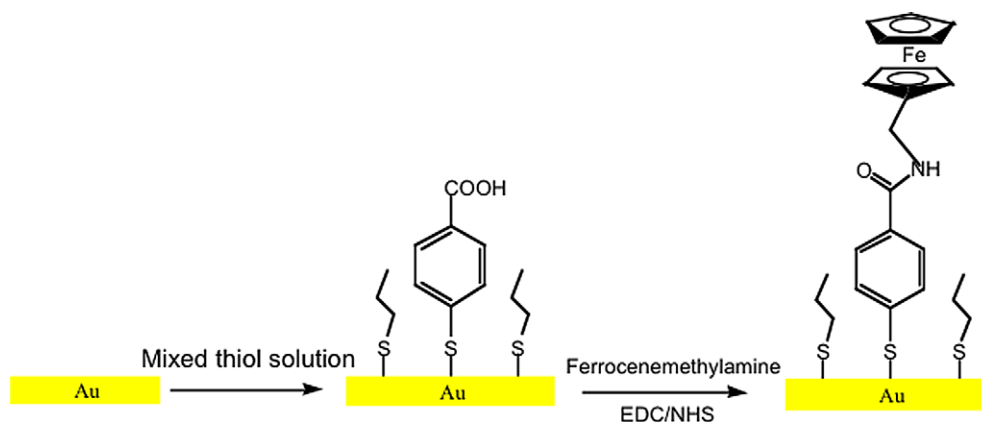
Poly-crystalline gold electrodes, prepared as described previously [28], were polished to a mirror-like finish with $1.0\ \mu\text{m}$ alumina, followed by 0.3 and $0.05\ \mu\text{m}$ alumina slurry on microcloth pad. After removal of trace alumina from the surface, by rinsing with water and brief cleaning in an ultrasonic bath with ethanol and then water, electrochemical cleaning in $0.05\ \text{M}$ H_2SO_4 by cycling the electrodes between -0.3 and $1.5\ \text{V}$ was carried out until a reproducible CV was obtained. Before derivatization, the cleaned electrodes were rinsed with water and dried under a stream of argon. The derivatization of gold electrodes with a mixture of diazonium salts was conducted in exactly the same manner as described for the carbon electrodes. The alkanethiol modified gold electrodes were prepared by immersing the gold electrodes in a $1\ \text{mM}$ mixed thiol solution (mercaptobenzoic acid and propanethiol with different dilution ratios) in ethanol overnight (see Scheme 2). The electrode was rinsed with copious amounts of ethanol, then water and finally dried under a stream of argon prior to the next step.

Covalent attachment of ferrocenemethylamine to carboxylic acid terminated monolayers followed the procedures described by Liu et al. [29]. The modified surfaces were incubated in an aqueous solution of $10\ \text{mM}$ *N*-hydroxysuccinimide (NHS) and $40\ \text{mM}$ 1-ethyl-3-(3-di-

methyl aminopropyl) carbodiimide hydrochloride (EDC) for $1\ \text{h}$. After the activation, the electrodes were rinsed with water and incubated in a $5\ \text{mM}$ ferrocenemethylamine solution in HEPES buffer pH 7.3 for $24\ \text{h}$.

2.3. Electrochemical measurements

All electrochemical measurements were performed with a BAS-100B electrochemical analyser (Bioanalytical System Inc. Lafayette, IL) and a conventional three-electrode system, comprising a GC or a gold working electrode, a platinum foil as the auxiliary electrode, and a Ag/AgCl $3.0\ \text{M}$ NaCl electrode (from BAS) as reference. All potentials were reported versus the Ag/AgCl reference electrode at room temperature. All CV measurements were conducted in pH 7.0 phosphate buffer. The area under the Faradaic peaks in the CVs of the ferrocene modified electrodes were used to determine the surface coverage of ferrocene. The rate constants for electron transfer were calculated from the variation in peak potential over a wide range of scan rates. For electrodes with prominent redox peaks the rate constants were determined by fitting the variation in peak potential with scan rate using the Marcus theory for electron transfer as described previously [30–32] whilst at low surface coverages of ferrocene the rates of electron



Scheme 2. Schematic of ferrocenemethylamine immobilized covalently on mixed monolayers of MBA and PT on gold surfaces.

transfer were determined using the Laviron [33] formalism. This was because peak shape and position was very sensitive background subtraction at with small redox peaks and therefore fitting the entire background subtracted CV peak as required for our Marcus simulation became unreliable. When both methods were employed on the same data very similar rate constants for electron transfer were obtained.

2.4. XPS measurements

XP spectra were obtained using an EscaLab 220-IXL spectrometer with a monochromated Al K α source (1486.6 eV), hemispherical analyzer and multichannel detector. The spectra were accumulated at a take-off angle of 90° with a 0.79 mm² spot size at a pressure of less than 10^{−8} mbar.

3. Results

3.1. Aryl diazonium salt modified glassy carbon electrodes

Glassy carbon electrodes were modified with diazonium salts via electrochemical reduction of an aryl diazonium salt (1 mM in acetonitrile) with 0.1 M tetrabutylammonium tetrafluoroborate as background electrolyte. The first sweep showed the characteristic reduction peak at −0.16 V versus Ag/AgCl with no associated oxidation peak indicative of the loss of N₂ and the formation of a 4-carboxyphenyl radical followed by covalent binding to the carbon surface [34]. Subsequent scans showed no electrochemistry indicative of a passivated electrode. The passivation of the GC surfaces after the modification with aryl diazonium salts was confirmed using potassium ferricyanide as a redox probe. Fig. 1 shows a cyclic voltammogram before and after modification with (4-carboxyphenyl) diazonium

tetrafluoroborate in 1 mM ferricyanide in a 0.05 M phosphate buffer (0.05 M KCl, pH 7.0) at a scan rate of 100 mV s^{−1}. After the modification of the surface with the aryl diazonium salts, the redox peaks of ferricyanide observed with bare GC electrodes were almost completely suppressed. This gave strong evidence that a uniform monolayer which blocked access of ferricyanide to the electrode had formed on the GC surfaces. Based on the area of the reduction peak during the modification of the GC electrode surface with the aryl diazonium salt, the coverage of the 4-carboxyphenyl moieties was calculated to be 7.4×10^{-10} mol cm^{−2}. The reported surface coverage on GC substrates varies in the range of $4\text{--}30 \times 10^{-10}$ mol cm^{−2} [35] with the theoretical maximum surface coverage [29] for a monolayer on GC surfaces being 12×10^{-10} mol cm^{−2}. The surface coverage of 7.4×10^{-10} mol cm^{−2} indicates the GC electrode was modified with a monolayer rather than multilayers of aryl groups as has been reported by some workers [36–38].

The modification of the GC electrode by electrochemical reduction of (4-carboxyphenyl) diazonium tetrafluoroborate was confirmed by X-ray photoelectron spectroscopy (XPS). Survey spectra showed the expected carbon 1s and oxygen 1s peaks at ~284 and ~532 eV, respectively, and also a small nitrogen 1s peak at ~400 eV (Fig. 2). The level of oxygen was increased in comparison to the bare GC surface as expected for the introduction of 4-carboxyphenyl groups onto the surface. The presence of the small nitrogen 1s peak in the survey spectra was partially due to nitrogen containing species already detectable on the unmodified GC electrodes, which has been observed previously [13,34]. Furthermore, nitrogen species with a binding energy of ~400 eV can be introduced onto the surface during the modification reaction. It has been proposed that these are due to a hydrazine generated by reaction of the diazonium salt with phenol groups on the GC surface [26].

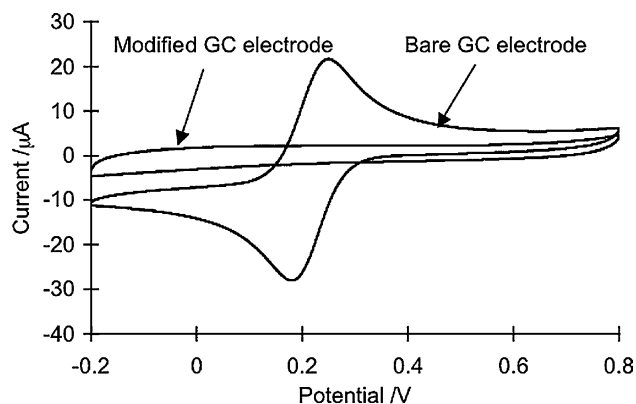


Fig. 1. Cyclic voltammograms before and after the modification of (4-carboxyphenyl) diazonium tetrafluoroborate on a GC electrode in a ferricyanide solution (1 mM KCl, 0.05 M phosphate buffer; pH 7.0) at a scan rate of 100 mV s^{−1}.

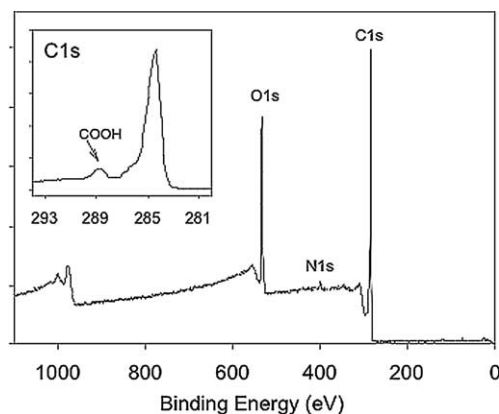


Fig. 2. XP survey spectrum and carbon 1s narrow scan (inset) of a GC electrode modified by electrochemical reduction of (4-carboxyphenyl) diazonium tetrafluoroborate.

Nitrogen 1s narrow scans (not shown) were consistent with the formation of low levels of the hydrazine, which exhibited a slightly different binding energy to that of the nitrogen species already present on the bare GC electrode.

The carbon 1s narrow scan (Fig. 2, inset) showed a peak centred at 288.8 eV, which was typical of the carbon of the carboxylic acid group [13]. This peak was absent from the carbon 1s narrow scan of unmodified GC surfaces. The carbon 1s peak at 284.4 eV was slightly broadened compared to the graphitic peak of an unmodified GC surface and was assigned to the graphitic carbon of the underlying GC electrode and the aromatic carbons of the monolayer. The pronounced asymmetry of this peak with a broad shoulder on the high binding energy side (~ 286.2 eV) was attributed to an oxidized species present on the GC surface and organic contaminants adsorbed on the monolayer.

After modification of the GC electrode surface with the aryl diazonium salt the next step in the fabrication of the modified electrodes was the attachment of ferrocene. CVs measured in an aqueous solution of 0.05 M phosphate buffer (0.05 M KCl, pH 7.0) at a scan rate of 100 mV s^{-1} before and after the immobilization of ferrocene on the 4-carboxyphenyl modified GC electrode are shown in Fig. 3. The strong redox peaks after the attachment of ferrocene showed linear variation in peak current with scan rate indicating that the ferrocene was surface bound. In the absence of EDC and NHS such that no covalent coupling of the ferrocene could occur, only very weak redox peaks due to physisorption were observed. The CVs of the ferrocene coupled to the 4-carboxyphenyl monolayers show non-ideal behaviour [1] with regards to peak separation at slow scan rates ($\Delta E_p = 79 \text{ mV}$ rather than the ideal $\Delta E_p = 0 \text{ mV}$) and

the full width half maximum (greater than 200 mV rather than the ideal $E_{\text{FWHM}} = 90.6 \text{ mV}/n$ where in this case $n = 1$). With regards to both peak separation and the E_{FWHM} the non-ideal behaviour has been attributed to the ferrocene molecules being located in a range of environments with a range of formal electrode potentials (E^0) [39,40]. We [29,41] and others [42] have noted previously that fabricating redox active SAMs by assembling the SAM and then attaching the redox molecule, results in broader FWHM than observed with electrodes where a redox active alkanethiol was attached directly to the electrode. The reason for modifying electrodes in this step-wise manner, where the monolayer is formed and then the redox active molecule attached, rather than synthesizing a pure redox active self-assembling molecule followed by assembly on the electrode, is because in applications of our interest, bioelectronics, the step-wise strategy is the only viable approach.

With a monolayer containing only 4-carboxyphenyl moieties the number of redox active molecules attached to the surface, as determined from the charge passed under the Faradaic peaks in the ferrocene modified electrode, is approximately $(0.073 \pm 0.012) \times 10^{-10} \text{ mol cm}^{-2}$ with a close to unity ratio of anodic to cathodic peak areas (see Table 1). Comparing the surface coverage of 4-carboxyphenyl groups of $7.4 \times 10^{-10} \text{ mol cm}^{-2}$, to that of the number of redox centres attached indicates that only approximately 10% of the 4-carboxyphenyl monolayers had a ferrocene attached. At this surface coverage the average area per ferrocene molecule, assuming homogeneous distribution, is 2.2 nm^2 which suggests there is a high possibility of interaction between redox active centres [29,42].

Interaction between redox active centres has been reported to decrease the reorganization energy and increase the electron transmission efficiency [4,43,44], hence providing an anomalously high measure of the rate constant for electron transfer. As a consequence, the number of coupling points within the monolayer that the ferrocene could couple was reduced by forming mixed monolayers composed of the 4-carboxyphenyl diazonium salt and the phenyl diazonium salt (Table 1). Table 1 shows that the surface coverage initially increased with the spacing of the coupling points followed by the more expected decrease as the number of coupling points decreased. The reason for the initial increase in surface coverage of ferrocene as the solution composition from which the monolayer forms changes from entirely 4-carboxyphenyl diazonium salt to a 1:1 ratio of 4-carboxyphenyl to phenyl diazonium salt is unclear. The percentage of carboxyl groups to be activated using EDC/NHS, as used here, in a SAM composed of entirely carboxylic acids has been shown to be approximately 50% [45] which is equivalent to all the 4-carboxyphenyl groups being activated in a 1:1 monolayer. Furthermore, the relative surface coverages of the 4-

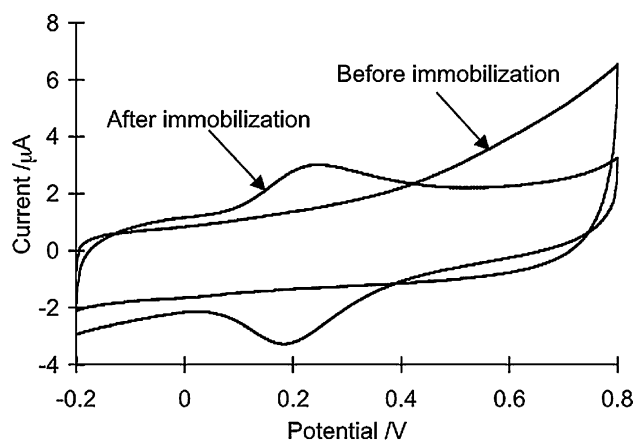


Fig. 3. Cyclic voltammograms before and after the coupling of ferrocenemethylamine onto the pure 4-carboxyphenyl modified GC electrode in 0.05 M phosphate buffer (0.05 M KCl; pH 7.0) at a scan rate of 100 mV s^{-1} .

Table 1

Some parameters of ferrocenemethylamine immobilized on GC electrodes modified with mixed monolayers of 4-carboxyphenyl and phenyl moieties. ΔE_p is recorded at a scan rate of 100 mV s⁻¹

[Benzyl]/[benzoic acid]	E^0 (mV)	ΔE (mV)	E_{FWHM} (mV)	Γ (pmol cm ⁻²)	Γ_a/Γ_c	k_{app} (s ⁻¹)
0	264 ± 15	79 ± 10	241 ± 10	72.8 ± 11.6	0.89 ± 0.07	17 ± 10
1	279 ± 13	78 ± 14	213 ± 19	100.3 ± 10.4	1.03 ± 0.04	28 ± 10
5	292 ± 9	89 ± 25	227 ± 25	67.4 ± 10.7	0.94 ± 0.05	15 ± 5
10	298 ± 7	93 ± 10	262 ± 38	48.1 ± 6.9	0.88 ± 0.11	16 ± 2
20	304 ± 17	101 ± 21	220 ± 29	29.4 ± 3.4	0.71 ± 0.16	15 ± 10
40	317 ± 19	107 ± 10	289 ± 14	13.3 ± 2.0	0.77 ± 0.13	10 ± 2

carboxyphenyl to ferrocene is 10:1 in the entirely 4-carboxyphenyl monolayer so there should be excess coupling points for the ferrocene to attach. Therefore, it is suggested that the introduction of a second component into the monolayer (the phenyl diluent) in effect introduces a hydrophobic component into the monolayer. As ferrocene has been shown previously to adsorb onto the surface of hydrophobic self-assembled monolayers [41,46]. Therefore, it is proposed that more ferrocene is attached when the phenyl component is introduced into the monolayer because the surface is more energetically favourable location for the ferrocene compared with an entirely carboxyphenyl monolayer.

The rate constant for electron transfer was determined from the variation in peak position between the anodic and cathodic scans as a function of scan rate. In this study, the variation in peak potential over a wide range of scan rates was fitted using the Marcus theory for electron transfer as described previously [30–32] rather than the Laviron [33] formalism which relies on simple Butler–Volmer kinetics and gives rate constants for electron transfer which are sensitive to the choice of sweep rates investigated. Table 1 shows that across the spectrum of dilution ratios investigated the rate constant for electron transfer (k_{app}) is approximately 15–20 s⁻¹.

3.2. Aryl diazonium salt modified gold electrodes

Gold electrodes were modified with aryl diazonium salts via electrochemical reduction in exactly the same manner to the GC electrodes. The reduction peak for the attachment of the aryl diazonium salt onto the gold electrode, observed in the first sweep, was shifted anodically 230 mV relative to carbon being at +70 mV versus Ag/AgCl. Subsequent sweeps showed no electrochemistry indicating a monolayer coverage of 4-carboxyphenyl moieties on the electrode surface. The 4-carboxyphenyl monolayer blocked access of potassium ferricyanide to the electrode in a similar manner to that depicted in Fig. 1 for the carbon electrode but to a lesser extent. The coverage of the 4-carboxyphenyl moieties on the electrode surface was 6.4×10^{-10} mol cm⁻² which was lower than the 7.4×10^{-10} mol cm⁻² observed on GC

electrodes and hence lower than the theoretical maximum surface coverage [34] for a monolayer of 12×10^{-10} mol cm⁻². The lower surface coverage could be a reflection of the aryl diazonium salt not being normal to the surface of the gold, as suggested by infra-red spectroscopy [20]. Again, the presence of a monolayer or submonolayer of aryl diazonium salt on the gold electrode is important due to the possibilities of obtaining multilayers with aryl diazonium salts as shown for both carbon [36–38] and metal surfaces [20].

An XP survey spectrum of gold modified with (4-carboxyphenyl) diazonium tetrafluoroborate showed the expected 1s peaks of carbon and oxygen at ~285 and ~532 eV, respectively, but no significant evidence of a nitrogen 1s peak (Fig. 4). The carbon 1s envelope (Fig. 4, inset) was fitted with four peaks at 288.7, 286.2, 284.6 and 283.9 eV assigned to the carboxylic acid moieties, C–O species, the aromatic carbons of the monolayer and the metal-bonded carbon, respectively. The binding energy observed for the carboxylic acid group on gold was consistent with that observed on the GC surface. The inclusion of the metal carbide peak is exceedingly tentative as a good fit to the spectra could be obtained without the presence of this peak. The assignment of the metal carbide peak is based on the

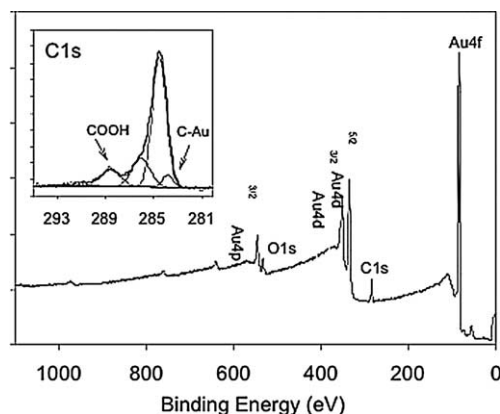


Fig. 4. XP survey spectrum and carbon 1s narrow scan (inset) of a gold electrode modified by electrochemical reduction of (4-carboxyphenyl) diazonium tetrafluoroborate.

precedence of Pinson and co-workers [19,20,47] who have previously proposed the existence of such a peak for the electroreduction of diazonium salts onto metal surfaces. On iron surfaces the case for a metal–carbide peak is compelling with a very pronounced shoulder when a high resolution instrument is used [47] with the intensity of this shoulder sensitive to take-off angle indicating it is a surface bound species. However, on copper electrodes [20] and other examples on iron [19] the shoulder on the carbon 1s spectra is less pronounced similar to the observations on gold here.

The electrochemical parameters after the attachment of ferrocene to the 4-carboxyphenyl modified gold electrodes are shown in Table 2. The trends were very similar to the GC modified electrodes with broader than ideal E_{FWHM} and non-ideal ΔE_p at slow scan rates. The surface coverage of ferrocene with different ratios of diluent to 4-carboxyphenyl were slightly lower than those on GC in common with the lower coverage in general of the aryl diazonium salts on gold compared with GC. Most importantly, the rates of electron transfer measured on the gold modified surface were significantly greater than that observed on carbon. Typically rates of more than a 100 s^{-1} were observed, which was approximately one order of magnitude higher than for the same monolayer system on GC electrodes. The values of the rate constants at the low surface coverage of ferrocene (last three entries in the table) were particularly difficult to determine because with small redox peaks background subtraction can have a large impact on the peak positions. As a consequence the rate constants quoted represent the lower limits and therefore we expect the true rate constant is closer to that observed at the 1:5 monolayer.

3.3. Aryl thiol modified gold electrodes

For comparison with the monolayers formed by electrochemical reduction of aryl diazonium salts we also prepared mixed monolayers of aryl thiol self-assembled monolayers on gold electrodes with attached ferrocene moieties as shown in Scheme 2. The rate constants determined for this equivalent aryl thiol system were in the order of 10^3 s^{-1} (at the limits of what can be measured

electrochemically) which was approximately 5–10 times the values observed for the aryl diazonium salt–gold system but two orders of magnitude higher than those observed for the aryl diazonium salt–GC system. These observations indicate that the metal surface has a significant effect on the rate of electron transfer.

4. Discussion

The rate constants for electron transfer are remarkably slower for the carbon electrodes relative to the gold electrodes. This is contrary to the suggestion that with diazonium salt modified carbon electrodes the continuity of conjugated carbon network from the electrode into the monolayer will result in a lower barrier for electron transfer than with organic monolayers on metallic electrodes [11]. The question that arises is why there is a difference in rate constants of around one order of magnitude for the same redox active molecule connected to electrodes by the same bridge molecule?

The Marcus–Hush expression for electron transfer between a donor and acceptor through an organic bridge in solution includes terms for electronic coupling between the donor and acceptor, the Gibbs free energy for electron transfer (the driving force, ΔG_{ET}) and the nuclear reorganization energy (λ) of the redox molecule as a consequence of its change in oxidation state [48]. For a given donor and acceptor pair the rate of electron transfer decays exponentially with distance according to a proportionality constant, the β value, sometimes called a damping factor. When the organic bridge is anchored to an electrode such that it can act as the donor and/or acceptor the situation is complicated somewhat as the electronic properties of the electrode can also play a role in the rate of electron transfer [2]. Equations describing the rate constant for electron transfer now incorporate terms related to the Fermi levels of the electrode and the effective density of electronic states near the Fermi level. In this study, the only changes between the monolayer systems studied relate to the electrode material and the bond to the electrode. Hence, the reorganization energy and the driving force will remain unchanged. The electronic coupling may be influenced by the electrode

Table 2

Some parameters of ferrocenemethylamine immobilized on gold electrodes modified with mixed monolayers of 4-carboxyphenyl and phenyl moieties. ΔE_p is recorded at a scan rate of 100 mV s^{-1}

[Benzyl]/[benzoic acid]	E^0 (mV)	ΔE (mV)	E_{FWHM} (mV)	Γ (pmol cm^{-2})	Γ_a/Γ_c	k_{app} (s^{-1})
0	268 ± 12	81 ± 14	209 ± 11	49.3 ± 7.6	0.87 ± 0.13	257 ± 41
1	277 ± 25	85 ± 9	191 ± 17	80.6 ± 5.9	0.86 ± 0.09	530 ± 42
5	280 ± 18	75 ± 10	227 ± 8	53.7 ± 5.4	0.72 ± 0.14	211 ± 23
10	282 ± 14	92 ± 12	260 ± 15	25.8 ± 4.0	0.92 ± 0.07	83 ± 50
20	292 ± 19	89 ± 8	272 ± 14	13.3 ± 2.4	0.76 ± 0.03	69 ± 50
40	317 ± 21	81 ± 16	308 ± 10	7.1 ± 1.0	0.93 ± 0.02	68 ± 50

material, as changes in electrodes may alter the extent of wave function mixing between the organic molecules and the substrates, especially when conjugated molecules are involved as in this case. A detailed discussion of the theory of electron transfer and how different electrode materials will influence the electron transfer is clearly not within the scope of our expertise. However, some comments on the large difference in the rate of electron transfer within the limited knowledge of the experimental systems investigated is worthwhile and may stimulate useful debate.

The first possibility is that there are multilayers on the carbon electrode rather than monolayers of the bridge molecule as the rate of electron transfer decays exponentially with distance. However, the surface coverage of the reduced aryl diazonium salts on the electrode, as determined from the charge passed, was below the maximum theoretical coverage for a monolayer of reduced aryl diazonium salts. This suggests a monolayer or submonolayer modification of the carbon electrode. Hence, any significant multilayering can be ruled out and the difference in electron transfer rate must, in some way, be related to the different electrode surfaces.

The different electrode surfaces could influence the rate of electron transfer due to the different electronic properties of the surfaces or the nature of the linkage made to each electrode or both. Our results support both of these possibilities playing a role. We draw this conclusion from the differences in rate constant calculated on the gold surface for the aryl diazonium salt relative to aryl thiol monolayers and the large difference the aryl diazonium salt derived monolayers on gold versus the carbon electrodes. The investigation of the aryl thiol monolayer systems on gold was necessary to draw this conclusion because of the uncertainty in the nature of the bond formed between the monolayer and the gold surface during the electroreduction of the aryl diazonium salt. On carbon electrodes a carbon–carbon covalent bond with little charge transfer is well established but the existence of a metal–carbon bond much less so. As indicated in the results section, the fitting of the C 1s spectrum with a metal carbide bond is tentative, as a good fit could also be achieved without including this bond. The suggestion of a metal–carbon bond is based on the precedence of Pinson and coworkers [19,20,47] who have provided good evidence for a metal carbon bond on iron and copper surfaces with very limited charge transfer [20]. That is a similar bond to that formed on a carbon electrode. The gold–thiol bond however, although also the subject of some controversy, is generally accepted as being a pseudocovalent bond with significant ionic character [49]. In our hands the rate constant for the gold–thiol system is at least five times that for the aryl diazonium derived monolayer on gold, despite the extra bond between the phenyl ring

and the electrode, which is the reason for the assertion that the bond to the electrode is playing some role.¹

If the bond between the organic monolayer and the electrode is only of minor importance when considering the large difference in rate constants between the gold and carbon electrodes, what is it about the electrode materials which cause such a large difference? For saturated bridge molecules in metal–molecule–metal junctions fabricated by assembling a monolayer on an electrode surface and contacting the top with a conducting probe atomic force microscope, Beebe et al. [50] have shown that the contact resistance is increased with increasing work function of the metals in the junction. Although GC is a heterogeneous material, the work function for carbon is approximately 5.0 eV whilst for polycrystalline gold it is 5.1 eV [51]. The similarity in the work-functions suggests this is not a dominant factor in the large difference in the rate constant for electron transfer. As a consequence, we propose the difference in rate constant is due to a difference in the electronic coupling between the electrode and the redox molecule, perhaps as a consequence of wave function mixing between the molecule and the electrode [52]. Stokbro et al. [53] have calculated for dithiol benzene assembled on a gold molecular break junction that when a gold–thiolate bond is formed the energies of the HOMO and LUMO of the dithiol benzene fall below the Fermi level of the organic molecule. Therefore, the electron density of the metal spills over into the organic molecule and both the HOMO and LUMO are occupied. A similar type of conclusion is arrived at by Hall et al. [54] for a molecular break junction with the same chemical system. Thus, we propose that spill over of electron density into the resultant monolayer derived from the aryl diazonium salts occurs on gold surfaces to a far greater extent than carbon surfaces and hence the rate of electron transfer is significantly greater.

The proposed chemical functionalities at the surface of polished GC electrodes include quinones, lactones, ketones, alcohols and carboxylic acids [16] as shown in Fig. 5A. The inference of Fig. 5A is that the delocalization of electrons throughout the carbon network is a consequence of an aromatic network of fused benzene rings. Radical attack by reduced aryl diazonium salts is expected to occur at electron rich centres such as carbons in the benzene rings and the carbons ortho to the

¹ Note we are not suggesting here that the carbon–carbon bond and the carbon–gold bond are identical, just that they are more similar than the gold–thiol bond. With the electroreduction of the aryl diazonium salt on either electrode material it appears that a covalent bond with limited charge transfer is formed between a phenyl ring and the electrode. In contrast, with the gold–thiol case a pseudocovalent bond is formed with an ionic character and a sulphur atom, which can provide a significant barrier to electron transfer [11], resides between the phenyl ring and the electrode.

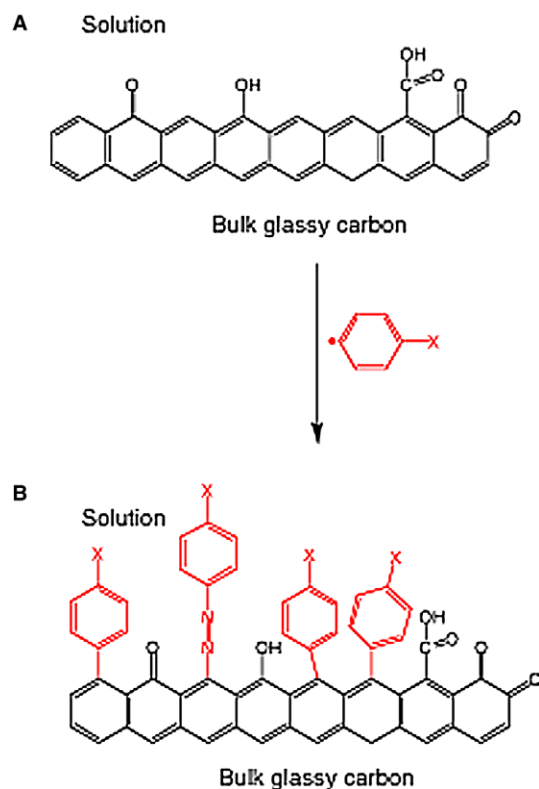


Fig. 5. Schematic of (A) a GC electrode showing the functional groups typically found on the electrode surface and (B) after modification with an aryl diazonium salt.

alcohols. Therefore, after attack by the aryl radicals the modified surface is expected to look like Fig. 5B. The hydrazine species proposed are observed in the XPS of the aryl diazonium salt modified carbon surfaces whilst no hydrazine species were observed after modification of the gold electrodes with the aryl diazonium salts as expected. Ignoring the hydrazine, which the XPS suggests is only a minor component of the surface, the carbon–carbon single bond between the bulk GC and the aryl rings from the diazonium salt suggests rather than a continuation of the aromaticity of the carbon surface, the coupling of the monolayer to this aromatic network by a single bond actually forms a barrier to the aromatic network. Biphenyl serves as an analogy to a phenyl diazonium salt coupled to a GC electrode, as it is one benzene ring connected to another benzene ring by a carbon–carbon single bond. Although aromatic biphenyl represents two effectively isolated aromatic rings with little or no delocalization of electrons between the rings. We propose therefore that with the carbon surfaces the mixing of delocalized electrons between the GC and the monolayer on the surface is unlikely to occur to a significant extent and hence there is a greater barrier to electron transfer than with the gold electrodes where electron density can spill over into the organic monolayer.

Evidence to support the notion that there is little mixing of delocalized electrons between a GC electrode and an aryl diazonium salt derived monolayer comes from Solak et al. [55]. Solak et al. [55] showed that a biphenyl diazonium salt modified GC electrode was effectively passivating to outer sphere redox active molecules in solution, a similar observation to Fig. 1. However, upon poisoning the electrode at -0.2 V, in which an electron is injected into the biphenyl ring, the organic layer deposited onto the GC electrode became conducting. Further layers of diazonium salts could be deposited and good electron transfer could occur to redox species in solution. Thus, the situation changed from the monolayer being a layer over the electrode to part of the electrode. It was proposed that the injection of an electron resulted in a change in the organization of π -bonds with a double bond connecting the GC electrode to the monolayer. Thus, the injection of the electron caused a significant decrease in the HOMO–LUMO gap, a reduction in the barrier to electron transfer and a higher electronic conductance. Thus, with the data presented in this paper, if on gold there is mixing of delocalized electrons between the gold electrode and the organic monolayer but little or no mixing of delocalized electrons on the GC electrodes there should be a difference in the amount of electron transfer that can be achieved with a redox active molecule in solution rather than attached to the monolayer.

The electrochemistry of the monolayer modified GC and gold electrodes with redox active molecule in solution are shown in Fig. 6. In both cases the electrode is modified with a 1:1 ratio of the carboxyphenyl to phenyl component. The two redox active molecules are ferricyanide in aqueous solution and ferrocene recorded in acetonitrile. These were chosen as they are both redox molecules which undergo outer sphere electron transfer rather than adsorbing onto an electrode surface prior to electron transfer occurring. Ferricyanide is negatively charged and may be repelled from the electrode surface by the carboxylate species at the electrode surface whilst ferrocene is neutral. Fig. 6 clearly shows diffusion controlled CVs where there is significantly more electron transfer through the monolayer on gold as distinct from carbon. This is particularly dramatic with the ferrocene redox couple where on gold the redox chemistry is identical to when the monolayer is absent. It is important to emphasize the ferricyanide electrochemistry was performed after the ferrocene measurements, verifying the monolayer is present. Thus assuming the packing of the diazonium salt derived monolayer is not dramatically different, and the similarity in surface coverage during deposition suggests the coverage of monolayer is similar on each electrode material, these results provide good evidence that the order of magnitude difference in electron transfer ability between aryl diazonium salt derived monolayer on gold and the same

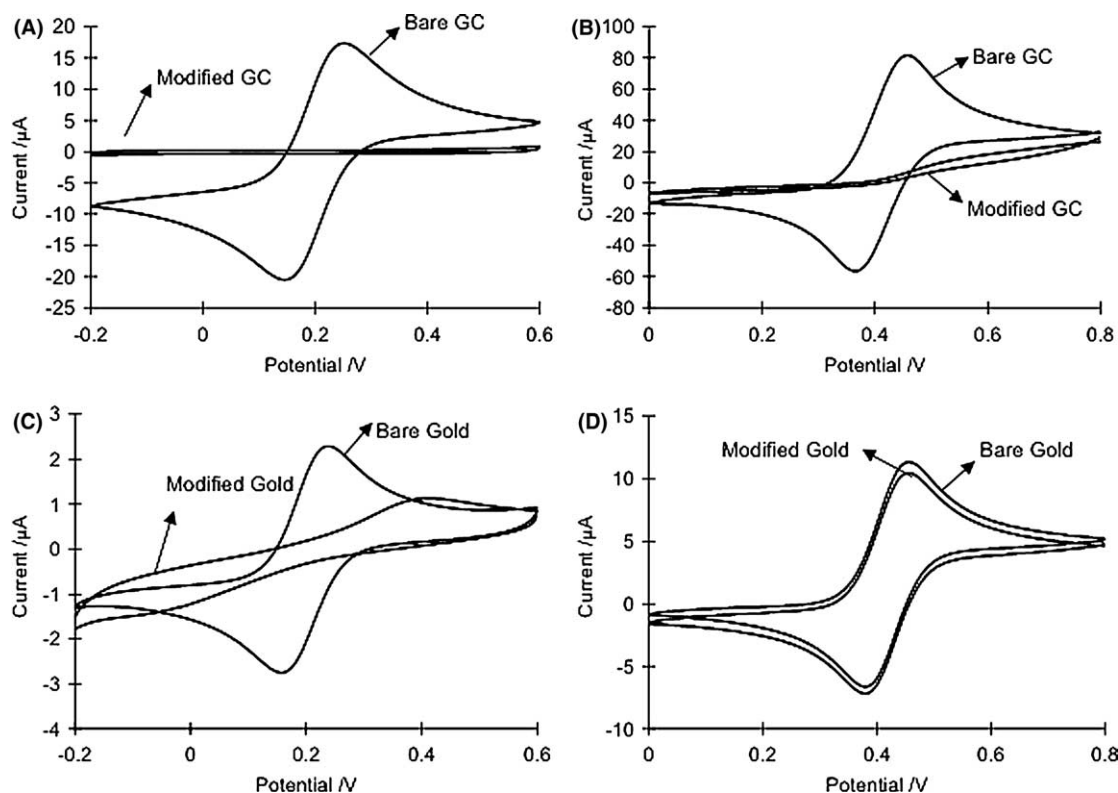


Fig. 6. Cyclic voltammograms of bare and modified electrodes with an outer sphere redox active species in solution. The electrodes were all modified with a 1:1 mole fraction ratio of 4-carboxyphenyl:phenyl diazonium salt. The electrodes are (A) GC electrode in a solution of 1 mM ferricyanide in 0.05 M potassium phosphate and 0.05 M KCl at pH 7.0, (B) GC electrode in 1 mM ferrocene acetonitrile with a background of 0.1 M tetrabutylammonium tetrafluoroborate (C) gold electrode in a solution of 1 mM ferricyanide in 0.05 M potassium phosphate and 0.05 M KCl at pH 7.0 and (D) gold electrode in 1 mM ferrocene acetonitrile with a background of 0.1 M tetrabutylammonium tetrafluoroborate.

monolayer on GC is due to better mixing of delocalized electrons on the gold surface.

5. Conclusions

Electrochemical reduction of mixtures of 4-carboxyphenyl and phenyl diazonium salts on GC and gold surfaces yielded stable monolayers to which ferrocenemethylamine could be covalently attached via activation of the surface bound 4-carboxyphenyl moieties. The rates of the heterogeneous electron transfer for immobilized ferrocene through the mixed monolayers were an order of magnitude higher for the gold electrodes in comparison to the GC electrodes. Furthermore, mixed diazonium salt derived monolayers on GC showed stronger blocking of electron transfer from redox-couples in solution than the equivalent monolayers on gold. These results suggest that the mixing of delocalized electrons between the electrode material and the monolayer occurs to a greater extent for gold than for GC allowing more rapid electron transfer for the system on gold than that on GC.

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