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Immobilisation of Alkylamine-Functionalised Osmium Redox Complex on Glassy Carbon using Electrochemical Oxidation

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ABSTRACT

The electrochemical oxidation of alkylamines provides a method for modification of carbon, and other surfaces via formation of a radical amine that reacts with the surface. Direct electrochemical oxidation of an alkylamine functional group of a redox complex provides a simple route to preparation of a redox active layer on carbon surfaces. Here we report on oxidation of an osmium redox complex, containing an alkylamine ligand distal to the metal co-ordination site, on carbon electrodes to directly produce a redox active film on the surface. The presence of the redox-active layer of osmium complexes is confirmed by cyclic voltammetry and X-Ray photoelectron spectroscopy. The average surface coverage of the attached film upon electrolysis of an [Os(2,2′-bipyridine)$_2$(4-aminomethylpyridine)Cl].PF$_6$ complex is 0.84 (± 0.3) × 10^{-10} moles cm^{-2}, demonstrating that coverages close to that predicted for a close-packed monolayer of complex is attained. The bioelectrocatalytic activity of the modified electrode was evaluated for oxidation of glucose in presence of glucose oxidase in solution. Hence, electrochemical coupling of alkylamine functionalised osmium redox complexes provides a simple and efficient methodology for obtaining redox active monolayers on carbon surfaces with potential applications to biosensor and biofuel cell device development.

1. Introduction

Modification of carbon electrode surfaces with redox layers is of interest to many application areas, such as biosensors, molecular electronics, biofuel cell devices and electrocatalysis [1,2]. Modification of surfaces can provide new properties to a surface while maintaining the bulk properties [3] with potential use for both analytical and chemical sensing [4]. The ability to form strongly-bonded, stable, monolayers on carbon surfaces is attractive for molecular device and sensor applications [5,6]. In addition, surface immobilised molecules which are capable of heterogeneous electron transfer between redox centre and surface can have high impact on the rapidly emerging field of high speed molecular electronics applications [7,8].

Various methods have been described for modification of carbon surfaces through a free radical grafting mechanism. For example, covalent modification of surfaces *via* reduction of aryldiazonium salts can lead to functionalised electrodes with high stability [2,9,10]. A major disadvantage to this approach is that synthesis and isolation of the diazonium salt is not always straightforward [11]. Apart from free radical grafting, formation of self-assembled monolayers (SAMs) using thiol chemistry on gold electrodes provides another way for introduction of chemical functionality to surfaces. However, the Au-thiol chemistry has several drawbacks such as thermal instability, prone to UV photo-oxidation [12] and mobility of layer results in a decreased electrochemical signal for many possible applications [10,13,14].

The covalent attachment of alkylamines to carbon and metallic surfaces using an electro-oxidation method has been reviewed in detail by Pinson and colleagues in recent years [15,16] and proven to be an excellent method for surface modification [17]. The extent of surface derivatisation depends upon the degree of substitution at the amine functionality [18], as tertiary amines show no evident surface coverage, compared to primary and secondary amines, proposed to be because of the steric hindrance which blocks the accessibility of amine radicals to surfaces [6,19].

Osmium and ruthenium based polypyridyl complexes are broadly explored for a range of applications as redox catalysts and mediators, due to the ease of synthetic variation of structure and therefore properties of these complexes [20]. For example, the redox potential of osmium based complexes can be tuned across a wide potential window by altering the ligand of a complex [21,22]. The favourable relatively low redox potential of osmium complexes and their relative stability in

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both oxidation states (II/III) is advantageous over the iron and ruthenium based systems [23]. Surface confined osmium based complexes are capable of mediating electron transfer to/from enzymatic [24,25] as well as microbial systems [26,27] on electrodes.

In the present paper, we report on direct grafting of an osmium complex, [Os(2,2′-bipyridine)$_2$(4-aminomethylpyridine)Cl].PF$_6$ (Osbpy4AMP), to glassy carbon and pyrolysed photoresist (PPF) surfaces by the simple methodology of electrochemical oxidation of the alkylamine functional group of the complex. Previously Buriez *et al.* [28] grafted a redox layer of amino-ferrocifen to carbon and metal surfaces based on electro-oxidation of the aryl-amine group of the organometallic complex, yielding strong attachment of the redox complex to surfaces [28]. Aramata *et al.* [29] grafted ligands of redox complexes onto carbon electrodes, using electro-oxidation of amine-containing ligands, to provide a platform for preparation of redox layers on carbon electrodes. Direct electro-oxidation of an osmium metal complex containing an aryl-amine ligand (4-aminopyridine) for grafting to carbon was also briefly described [29]. More recently, osmium polypyridyl complexes have been grafted to carbon surfaces to provide redox layers capable of mediating electron transfer to a glucose-oxidising enzyme in solution [30]. Details of the direct grafting of Osbpy4AMP to carbon surfaces by simple electro-oxidation of the alkylamine group is reported on here. The resulting modified surface is characterised by cyclic voltammetry (CV) and X-ray Photoelectron Spectroscopy (XPS). The experimental results demonstrate that a monolayer of redox complex is formed that is stable and can be used as a mediating surface for glucose oxidation by glucose oxidase in solution. Use of this chemical coupling methodology can provide a simple route for modification of a surface with a variety of osmium redox complexes for application to biosensor and biofuel cell device development.

2. Experimental

All chemicals were purchased from Sigma-Aldrich and used without any further purification. All solutions were prepared in Milli-Q (18.2 MΩ cm) water unless otherwise stated. Either glassy carbon disk (GC, 3 mm diameter) or plate (25 × 25 × 1 mm) working electrodes were used along with a platinum wire counter electrode and an Ag/AgCl (3 M KCl) reference electrode in a 10 mL single compartment electrochemical cell (all sourced from IJ Cambria). The pyrolysed photoresist (PPF) working electrodes (approximately 15 mm × 15 mm) were a gift from Alison Downard, University of Canterbury. The PPF were fabricated using two coats of photoresist which were spin coated onto silicon wafer followed by soft baked before pyrolyzing at 1050 °C [31,32]. For the modification of PPF surface, the electrodes were mounted on an insulated metal stage with four springs. A hole in the bottom was positioned on top of a Viton O-ring that sealed the solution above the electrode. Phosphate buffered saline (PBS), pH 7.4, was prepared using 50 mM phosphate buffer with 0.1 M NaCl. Glucose oxidase type VII from *Aspergillus niger* (GOx, EC 1.1.3.4., average activity 180 unit/mg) was purchased from Sigma-Aldrich.

[Os(2,2′-bipyridine)$_2$(4-aminomethylpyridine)Cl].PF$_6$ was synthesised according to literature methods [33] based on the 4-aminomethylpyridine (4-AMP) ligand substitution of a chloride by heating an ethylene glycol solution of a 1.1 mole equivalent ligand and Os(2,2′-bipyridyl)$_2$Cl$_2$ complex at reflux, with precipitation of the resulting complex by addition of an aqueous NH$_4$PF$_6$ solution [34]. Final product was filtered and allowed to dry overnight at 50 °C. Microanalysis for [Os(2,2′-bipyridine)$_2$(4-aminomethylpyridine)Cl].PF$_6$: C, 39.86%; H, 3.25%; N, 10.23% compared to theoretical values: C, 39.47%; H, 3.06%; N, 10.62%.

Prior to modification, GC disk electrodes were polished with 1 μm, 0.3 μm, and 0.05 μm of alumina slurry on microcloth pads (Buehler) followed by rinsing with Milli-Q-water and drying with nitrogen gas stream. The glassy carbon plate and PPF electrode were cleaned by sonicating in acetonitrile for 15 minutes. All experiments were carried out at room temperature unless otherwise stated.

2.1. Apparatus

All electrochemical measurements were performed using a CHI 620 potentiostat in a conventional three electrode cell. XPS was carried out using a Kratos AXIS 165 spectrometer with the following parameters: Sample Temperature: 20-30 °C, X-Ray Gun: mono Al Kα 1486.58 eV; 150 W (10 mA, 15 kV), Pass Energy: 160 eV for survey spectra and 20 eV for narrow regions. Step: 1 eV (survey), 0.05 eV (regions), Dwell: 50ms (survey), 100 ms (regions), Sweeps: survey (4), narrow regions (5-20). For calibration the C 1s line at 284.8 eV was used as charge reference for determining binding energies. Other spectra were collected in the normal to the surface direction. XPS detection limit is estimated to be ~0.1 at%. Quantitative survey spectra were obtained on high resolution spectra of elements acquired. The measurements were taken at take-off angle of 30° (sample tilt 60°) for better surface sensitivity.

3. Results and discussion

3.1. Electrochemically induced attachment of alkylamine functionalised redox complex to carbon surface.

Prior to surface confinement, solution phase cyclic voltammetry (CV) is used to evaluate the redox potential for the Os(II/III) transition of the Osbpy4AMP complex. Characteristic oxidation and reduction peaks are observed centred at 0.34 V (vs. Ag/AgCl), Fig. 1a, for 0.1 mM Osbpy4AMP in acetonitrile solution containing 0.1 M tetraethylammonium tetrafluoroborate as electrolyte. A formal potential of 0.30 V vs. Ag/AgCl can be estimated for the Os(II/III) transition from CV in aqueous phosphate buffer (pH 7.4); a value that is similar to that observed by others for the complex in buffer solution [35]. The electrochemically induced attachment of Osbpy4AMP to carbon surfaces was performed via oxidation of the alkylamine functional group of the complex, in acetonitrile solution containing 0.1 M of tetraethylammonium tetrafluoroborate as electrolyte. The consecutive cyclic voltammograms of 0.1 mM Osbpy4AMP show a broad electrochemically irreversible peak appearing at around 1.9 V vs. Ag/AgCl in the potential window from 1.5 to 2.1 V. The peak current decreases with multiple voltammetric scans recorded at 0.1 Vs^{-1}. This peak is attributed to the one electron electrochemical oxidation of the alkylamine with formation of an amine radical that can covalently couple to glassy carbon and pyrolysed photoresist (PPF) surfaces, as depicted in Scheme 1. Under continuous cycling the magnitude of peak current decreases, as observed by others [6,18], and as shown in Fig. 1(b). This is proposed to be as a result of a decrease in availability of surface area for coupling once the first scan, and coupling process, is undertaken [6,18], thus indicating coupling reaction at electrode surfaces [15,17,36]. The redox potential for the oxidation is in agreement with data for oxidation of alkylamines and mono-Boc-protected diamine compounds at glassy carbon electrodes [6,17,37].

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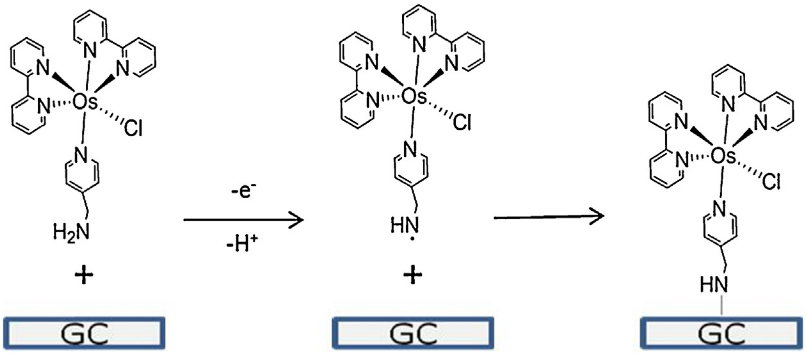

Scheme 1. Scheme depicting the proposed mechanism for electrochemically induced coupling of Osbpy4AMP to a glassy carbon surface.

3.2. Characterization of redox complex modified surface

Cyclic voltammetry can be used to evaluate if the redox complex is surface confined. The modified surface was cleaned with ultrapure millipore water, sonicated for 2 minutes and then voltammograms recorded in 0.05 M of phosphate buffer saline (pH 7.4), Fig. 2a. The redox potential for the Os(II/III) transition is 0.3 V vs Ag/AgCl similar to that for the complex in solution and coupled to adsorbed electrode films or to graphite electrodes [35,38,39], indicating that the redox potential of the Os(II/III) transition is generally not affected by immobilisation [21]. The anodic and cathodic peak currents increase linearly with scan rate, as expected for a surface-confined redox species, Fig. 2b [40].

The CVs of the surface bound complex at pH 7.4 in PBS shows non-ideal peak separation, greater than zero, particularly at higher scan rates, and a full-width at half-maximum of 160 mV, greater than the value for an ideal monolayer of a redox complex on an

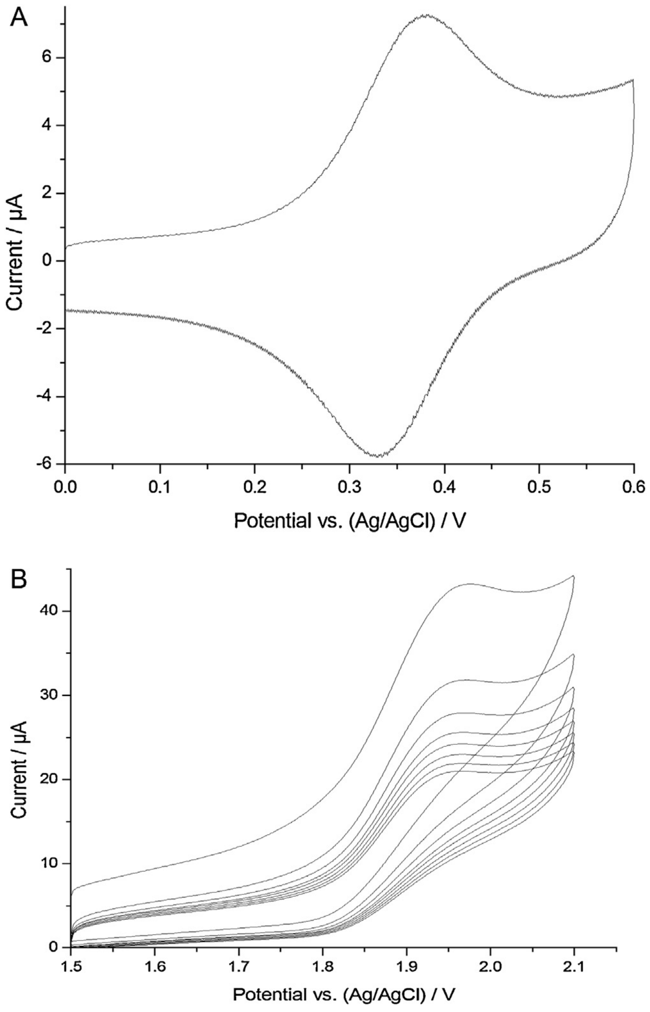

Fig. 1. Cyclic voltammograms of solution of 0.1 mM [Os (2,2′-bipyridine)$_2$(4-aminomethylpyridine)Cl].PF$_6$ in 0.1 M TEATFB in acetonitrile at a scan rate 0.1 Vs^{-1} (a) with a potential window selected to show the Os(II/III) transition and (b) the electrochemical oxidation of the alkylamine (8 repeated cycles).

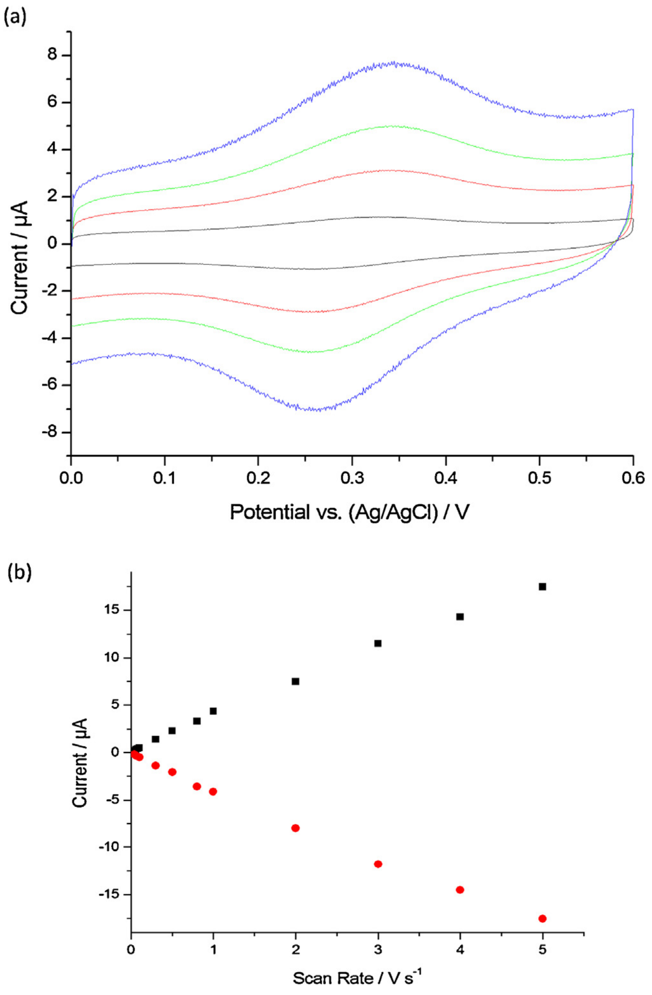

Fig. 2. (a) Cyclic voltammograms of a modified glassy carbon electrode in 0.05 M PBS (pH 7.4) at scan rates of 10 (black), 30 (red), 50 (green) and 80 (blue) mVs^{-1}. (b) Plot of anodic and cathodic peak current, extracted from cyclic voltammograms of a modified glassy carbon electrode, versus scan rate (Vs^{-1}).

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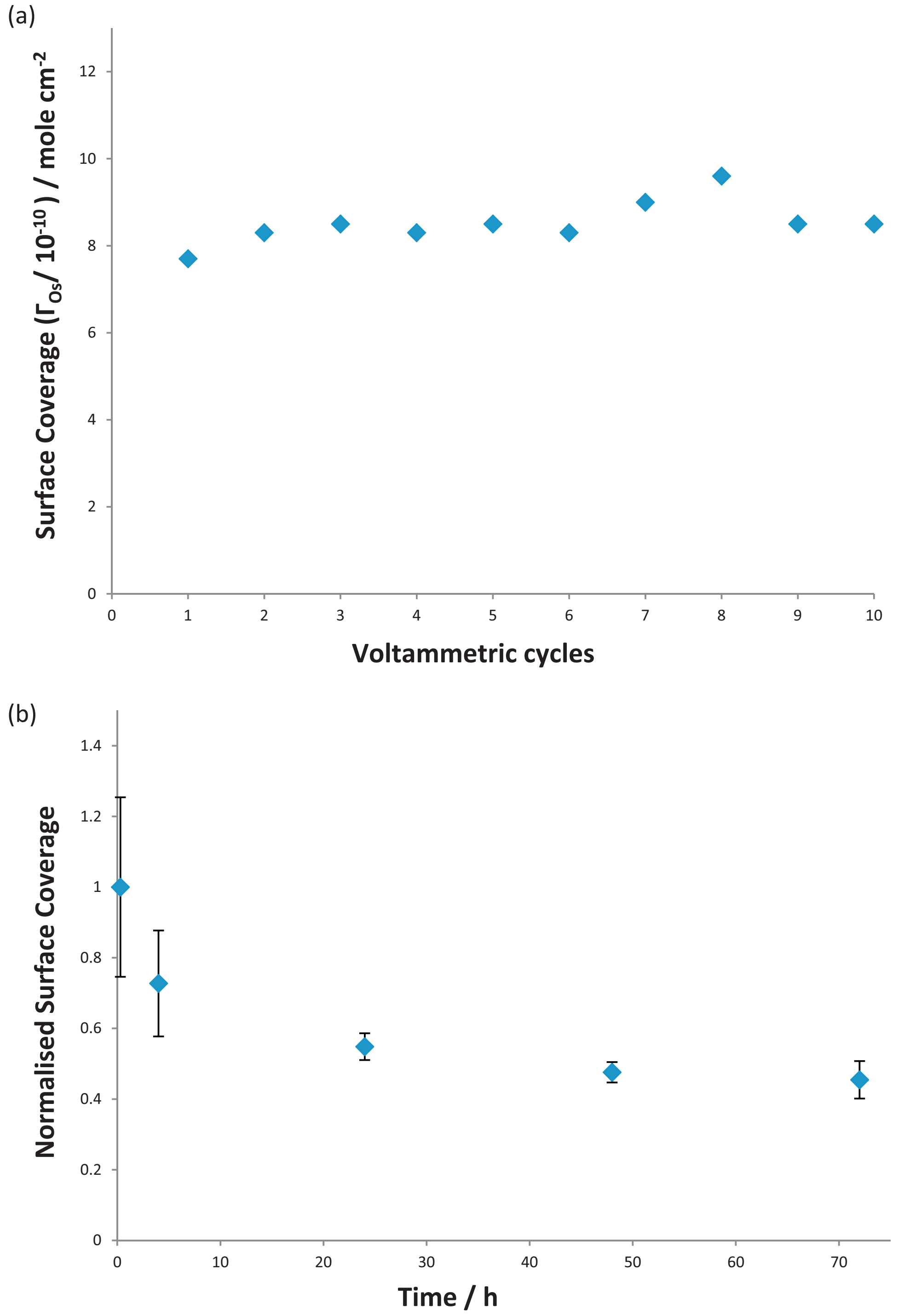

Fig. 3. Surface coverage of osmium complexes calculated from cyclic voltammetric peaks of modified glassy carbon electrodes at 0.1 Vs^{-1} scan rate in 0.05 M PBS buffer (pH 7.4) as a function of (a) continuous voltammetric cycling and (b) a single voltammetric cycle with storage of electrode in buffer (pH 7.4) at room temperature between scans.

electrode surface [40]. This deviation may be attributed to a combination of lateral interactions within the films [41]. The surfaces coverage (Γ_{Os}) of osmium can be calculated by integration of the charge passed under the oxidation peak (after baseline correction):

$$\Gamma_{Os} = Q/nFA \quad (1)$$

Where Q is the charge, F is the Faraday constant, n is number of electrons transferred, and A is area of the electrode.

The average Γ_{Os} value obtained from modified electrodes, prepared by cycling for one, three, or five cycles at 0.1 Vs^{-1} from 1.5 to 2 V, is 0.75 (± 0.2) × 10^{-10} moles cm^{-2}. No trend in Γ_{Os} as a function of the number of CV cycles used in the preparation method is apparent. Electrochemical grafting under these conditions is thus independent of the number of cycles used. This is in agreement with a report that electrografting of primary alkyl amines to carbon surfaces through repetitive cycling or scanning to more positive potential ranges does not increase the surface coverage, as calculated from the N/C value using XPS [18]. Moreover, the final surface coverage of osmium complex does not scale with scan rate, in the range 0.06 Vs^{-1} to 0.5 Vs^{-1} when three CV cycles are used

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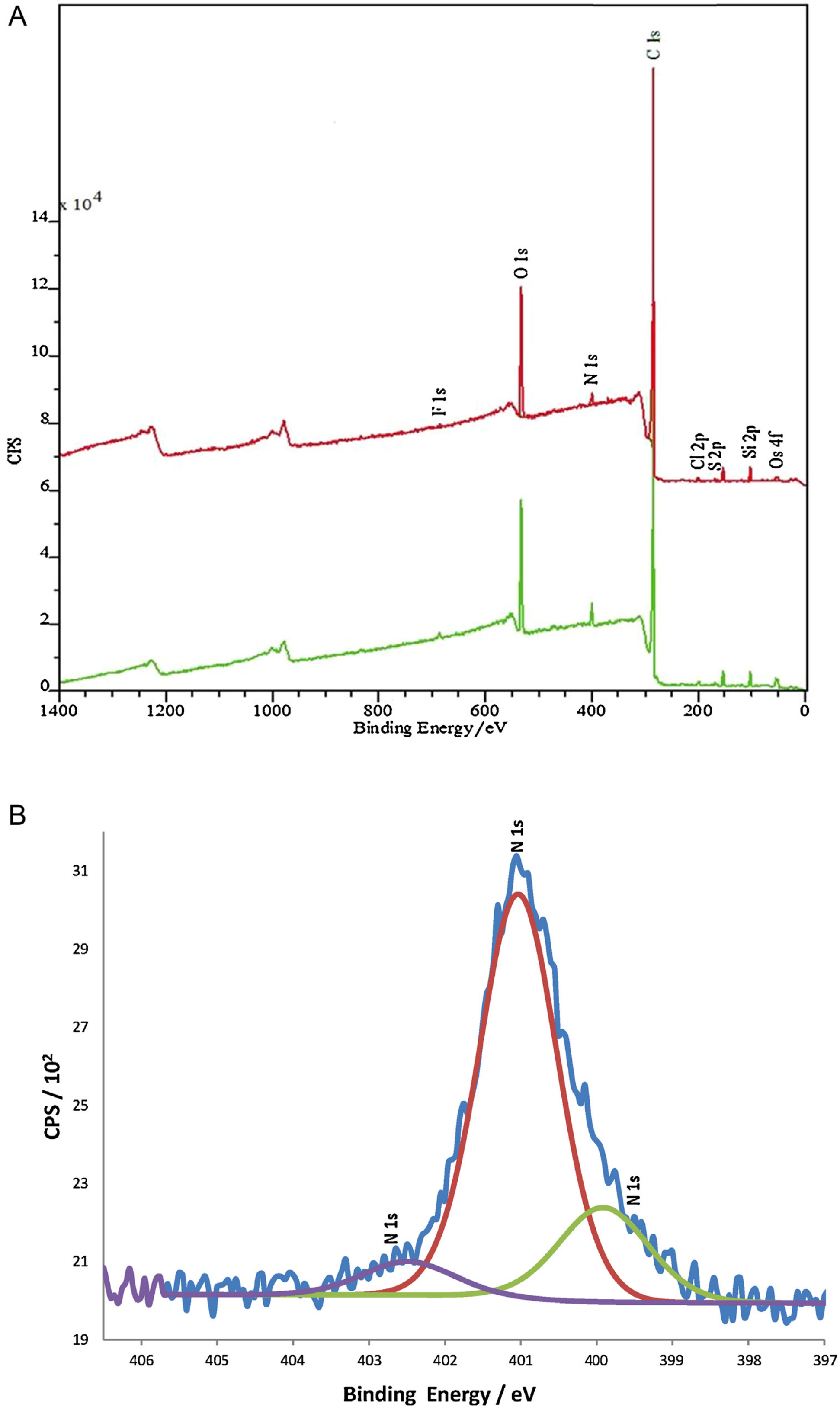

Fig. 4. XPS survey scans (a) at 30° (red) and 60° (green) and (b) N1s core fitting peak of a glassy carbon plate surface modified electrode by grafting of Osbpy4AMP.

for electrochemically induced coupling of the complex to carbon electrodes, with an average Γ_{Os} of $0.84\,(\pm 0.3) \times 10^{-10}$ moles cm^{-2}.

Integration of the charge for amine oxidation, for the lowest charge passed for one cycle at 0.5 Vs^{-1} gives an estimate of 2.0×10^{-6} C the equivalent of 2.1×10^{-11} moles of amine electrolysed in a one-electron oxidation, that results in formation of a layer on the electrode surface comprised of 6.7×10^{-12} moles of the osmium complex corresponding to surface coverage of

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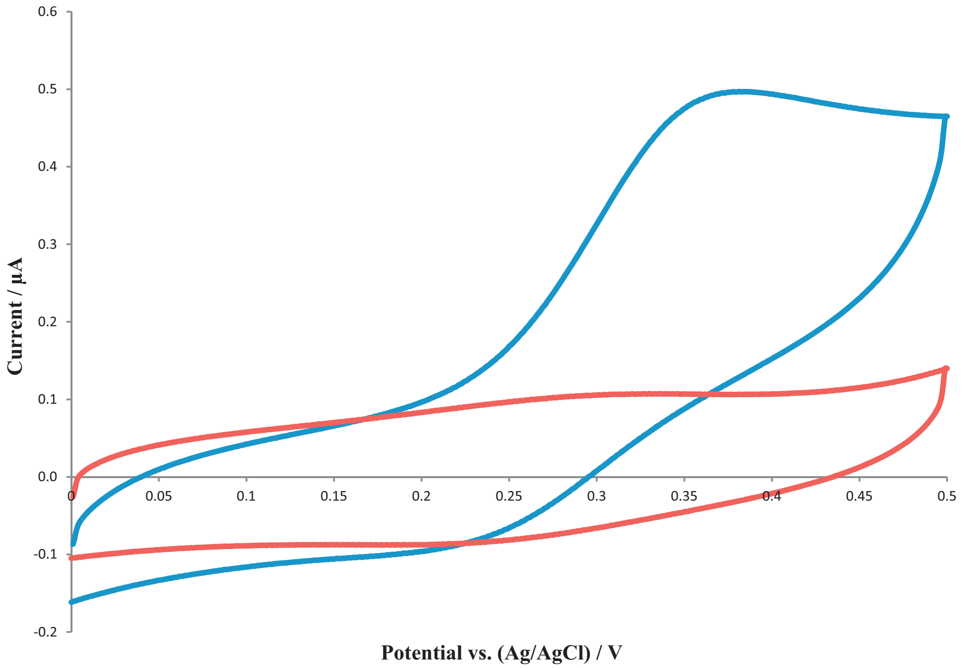

Fig. 5. CV recorded at modified, by electrografting Osbpy4AMP, glassy carbon electrode in 0.5 ml PBS buffer (0.05 M, pH 7.4, 37 °C) containing glucose oxidase (9 U) in the absence (red curve) and in the presence (blue curve) of 0.1 M glucose, at a scan rate of 5 mV s^{-1}.

0.9×10^{-10} moles cm^{-2}. The primary amine radical cations formed after electro-oxidation are reportedly more unstable [17], thus more reactive, compared to secondary or tertiary amines, thus suggesting that passage of lower charge in the electro-oxidation may be necessary to probe for an effect on final surface coverage of the osmium complex.

From the average osmium complex surface coverage of 0.84 ($\pm$ 0.3) $\times 10^{-10}$ moles cm^{-2} an area per molecule of osmium complex of approximately 197 $Å^2$ can be estimated, presuming complete monolayer coverage on a smooth surface. This is in reasonably good agreement with a projected area of 180 $Å^2$ estimated from crystallographic data, considering a radius of osmium polypyridyl complexes of 7.5 Å [42]. For comparison, an area per molecule of osmium polypyridyl complexes self-assembled as a monolayer on platinum electrode surfaces of approximately 240 $Å^2$ was reported, with a redox complex surface coverage of 1×10^{-10} moles cm^{-2} [43]. Thus, the proposed electrochemical coupling procedure produces a relatively compact redox active layer, at close to monolayer coverage. Multilayer formation may be possible, but given the surface coverage is not likely, as reported on by others for surface grafting via electro-reduction of aryl diazonium salts [9,38,44]. The osmium surface coverages reported here are in good agreement with surface coverages reported for monolayers of osmium complexes self-assembled on platinum and gold [10,37,38,43] and a surface coverage of 3.5×10^{-10} moles cm^{-2} for attachment of a ferrocene complex to a bromophenyl-modified carbon electrode [45] and to a surface coverage of 2.1×10^{-10} moles cm^{-2} for attachment of a copper complex to a gold surface using an aryldiazonium salt reduction method [46], while Boland *et al.* reported that attachment of the Osbpy4AMP osmium complex to a carboxylic acid-terminated carbon electrode using carbodiimide coupling yielded a surface coverage of 2.9×10^{-10} moles cm^{-2} [10]. For comparison, Buriez *et al.* [28] reported the surface coverage of 2.7×10^{-10} moles cm^{-2} for amino-ferrocifen complexes while Aramata *et al.* [29] reported a surface coverage of 1.7×10^{-10} moles cm^{-2} for grafting of an arylamine osmium complex on carbon surfaces.

The short term stability of the osmium complex at the surface is tested by undertaking repetitive CV cycles (Fig. 3a) at 0.1 Vs^{-1} scan rate in 0.05 M PBS buffer, with no change in the osmium surface coverage over the 10 cycle testing period. Longer-term stability to storage conditions is estimated from cyclic voltammograms recorded in buffer with storage intervals in buffer solution under room temperature, Fig. 3b. In this case, initially there is a loss in redox signal of immobilised complex of approximately 27% over a 4 hour period. This may be attributed to the loss of physisorbed molecules, as the decay profile does not follow a simple single-exponential fit, indicating that more than one process, or population of redox complex, may be responsible for the change in surface coverage as a function of storage time. Following this initial change, the surface coverage signal remains steady, losing only an average of 17% of the signal at 4 hours over the next 70 hours of storage.

The XPS results recorded after grafting of the osmium complex to glassy carbon plates confirms the presence of the complex on the surface. The survey scan of the modified glassy carbon surface, prepared by cycling for 3 cycles over a potential range from 1.5 to 2.0 V *vs.* Ag/AgCl in 1 mM Osbpy4AMP dissolved in ACN at 0.1 Vs^{-1} is shown in Fig. 4a. The spectrum exhibits the characteristic peaks for C 1s, N 1s and O 1s at 284.21, 400.5 and 532.21 eV, respectively. The presence of N, Os, and Cl XPS peaks for the modified surface is a clear indication that the Os complex is present on the carbon substrate. The peak F 1s at 685 eV corresponds to the fluoride (PF_6) present in the osmium complex salt. The Si 2p peak at 102 eV is assigned to adventitious substrate impurities, as reported on previously for XPS of carbon surfaces [47,48]. The origin of the S 2p peak at 167 eV is not as yet identified, but may also likely have arisen by adventitious substrate contamination. The high resolution XPS scan of the N 1S region, Fig. 4b, for the modified electrode surface shows a peak at 399.6 eV, has been attributed to the N in bipyridine [49,50], while the component close to 400.5 eV is reported to correspond to an amine functional group. The higher energy peak around 402.0 eV may be due to protonation of the amine during the grafting process [17]. The atomic % ratio of N 1s/C 1s, after correction for instrumental sensitivity is 0.044, compared to a reported ratio for bare glassy carbon of 0.014 [6] once again providing evidence of the presence of the complex at the surface.

3.3. Bioelectrocatalysis for glucose oxidation

Osmium redox complexes are commonly used as mediators in research and development of glucose biosensors [12,51] and glucose oxidising enzymatic biofuel cells [35,52]. Clark *et al.* developed the first enzyme based amperometric electrode in 1961 [42], and since then enzyme based electrode sensors have received great attention for application to glucose detection. As the redox active site of glucose oxidase is buried inside the insulating protein shell it is difficult to capture electron flow from the active site of enzyme as a result of glucose oxidation, to deliver them to the electrode, in so-called third generation biosensors devices [52]. The redox mediator is used, in second generation glucose biosensors, to shuttle electrons from the enzyme active site to the electrode surface. Redox mediator utilisation in enzyme-based electrodes allows for increased sensitivity, selectivity, and detection of analyte at lower overpotentials in many applications ranging from industry, environmental, energy to clinical applications [12,24,52].

The electrode surface modified by electrografting of an osmium complex was therefore examined in a preliminary test for its ability to mediate electron transfer from glucose oxidase, in solution, as a result of glucose oxidation. The response of the osmium complex modified electrode was evaluated using slow scan cyclic voltammetry in phosphate buffer solution (pH 7.4, 37 °C), Fig. 5. The modified electrode exhibited in the absence of substrate a CV signal with a pair of redox peaks centred at 0.3 V vs Ag/AgCl, indicating the presence of the osmium complex on the surface. Upon addition of glucose at saturation levels (0.1 M in the electrochemical cell), the cyclic voltammetric response altered with an increase in the oxidation current accompanied by a decrease in the reduction current, corresponding to a catalytic response [20,40], demonstrating the possibility of using the electrografting methodology to prepare, and compare, a range of redox complex modified electrodes for screening for application to biosensor or biofuel cell device development.

4. Conclusion

Carbon electrode surfaces are modified via electrochemical coupling of an alkylamine functional group of an osmium-based redox complex in a simple procedure. Cyclic voltammetry and XPS data indicates the presence of the osmium complex at the surface. The modified electrode showed electrocatalytic activity for oxidation of glucose in presence of glucose oxidase. The same modification strategy may be extended to provide a simple route for immobilisation of a range of redox complexes that possess an alkylamine functional group distal to the central metal atom to explore the effect of structure and complex redox potential on the surface coverage of complex and electrocatalytic applications of the resulting redox layers. For example, the modified surfaces could have application in a wide range of biosensor and biofuel cell electrochemical devices, as well as exploring the use of redox layers for light-harvesting or water-splitting applications.

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