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Electrochemical and Spectro-electrochemical characterization of graphene electrodes derived from solution-based exfoliation

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Dedicated to Prof RG Compton on the occasion of his 60 birthday - "60 and not

out?"

## ABSTRACT

Solution phase exfoliation of graphite to yield multi-layer graphene is used to form transparent electrodes, when transferred to polymer substrates. The electrochemical performance of these electrodes is determined and their use as optically-transparent electrodes for spectro-electrochemical applications is described.

## Keywords

Graphene, spectroelectrochemistry, exfoliation, OTTLE, electroanalysis.

## Introduction

Optically transparent electrodes (OTEs) ideally provide conductive platforms with excellent spectral transmittance. These properties are pre-requisites for spectroelectrochemical studies but are also requirements for suitable substrates for thin-film optoelectronics<sup>1</sup>, such as photovoltaics and organic light-emitting diodes<sup>2</sup>. Commercially available OTEs, mostly based on metal oxides, are expensive or contain toxic material and this has driven a surge of recent activity in carbon-based OTEs, in particularly carbon nanotube (CNT) networks<sup>3 4</sup>, as alternatives to metal oxide or metal film electrodes<sup>5</sup>. Graphene represents another promising carbon allotrope that can be processed to produce transparent and conductive films<sup>6 7 8 9</sup> owing to its high electron mobility and favourable optical properties. Reduced graphene oxide has been used in the specific context of OTEs in spectroelectrochemistry<sup>1</sup>, however graphene is expected to give improved performance due to its superior conductivity compared to graphene oxide. A number of methodologies are available for graphene production<sup>10</sup>, namely mechanical exfoliation<sup>11</sup>, chemical vapour deposition<sup>12 13</sup>, chemical reduction of graphene oxide <sup>14</sup>, <sup>15</sup> and the unzipping of CNTs to form graphene nanoribbons <sup>16, 17</sup>. Another route is *via* liquid exfoliation, whereby aqueous<sup>18</sup> <sup>19</sup>, organic<sup>20</sup> or mixed<sup>21</sup> graphene suspensions are prepared through the application of ultrasound, and depending on the solvent used and sonication conditions chosen, the graphene dispersions can have optimum concentrations ranging from 0.01 to 2.0 mg mL<sup>-1</sup> <sup>22</sup> <sup>23</sup>. Aqueous dispersions are usually stabilized by surfactants<sup>24</sup> or polymers<sup>25</sup>, which can interfere with electrochemical measurements<sup>26</sup> rendering them unsuitable as OTEs. Organic dispersions also present challenges, since the most effective solvents have high boiling points, which impede solvent removal from fabricated films. To date, electrodes fabricated from organic-based exfoliations include the use of pyridine, N,N-dimethylformamide (DMF) and chloroform as solvents<sup>27</sup> <sup>28</sup> <sup>29</sup> <sup>22</sup>. However, N-methyl-2-pyrrolidone (NMP) has been identified as a more effective solvent for liquid-phase exfoliation<sup>30</sup>, as its interfacial energy more closely complements the surface energy of graphene and has been shown to produce metastable dispersions with significant amounts of monolayer flakes.

Much debate has centered on the electrochemical properties of graphene and the relationship between the method of fabrication and electrochemical response. A diagnostic of voltammetric performance is the peak separation,  $\Delta E_{\rho}$ , and for the  $[Fe(CN)_6]^{3^-/4^-}$  redox couple at a scan rate of 100 mV s<sup>-1</sup> the following  $\Delta E_{\rho}$  values have been reported: 65 to 80mV for an electrode based on reduced graphene oxide  $(rGO)^{31}$ , 120 mV for an electrode based on graphene exfoliated in DMF<sup>28</sup> and 87 mV for an electrode based on the methylene blue assisted exfoliation of graphene in aqueous solution<sup>19</sup>. The origin of these differences in  $\Delta E_{\rho}$  is uncertain, but could be due to the presence of impurities introduced during fabrication, from functional groups which are formed on the surface or edges of the graphene sheets<sup>32</sup>.

Such properties are also affected by the method used to transfer the graphene onto a substrate or electrode. The first electrochemical studies of graphene materials were based on glassy carbon electrodes<sup>31 33</sup>, in these cases the final electrodes were modified by casting rGO suspensions onto the glassy carbon electrode surfaces followed by evaporation of the solvent. In fact, rGO modified electrodes have been widely studied<sup>34 35</sup>, in contrast graphene-based electrodes derived from liquid-phase exfoliation are far less prevalent in the literature. This can be understood by considering the inherent difficulties associated with removing high boiling point solvents (*vide supra*) from graphene films.

In this manuscript, we report the fabrication and characterization of optically transparent electrodes formed from bilayer to multi-layer graphene (MLG) flakes, prepared by liquid exfoliation in NMP. Considerable efforts have been made recently to prepare transparent electrodes from carbon-based materials, either for applications in photovoltaics<sup>36</sup> or with more fundamental exploration of the properties of conducting forms of carbon, including CNTs<sup>37 38</sup>, in mind. Here we present a method based on a previously reported technique for transferring CNT solutions onto polyethylene terephthalate (PET) substrates<sup>39</sup>, which has been adapted to the MLG case by partially exchanging NMP for the lower boiling point solvent 1,2-dichloroethane (DCE), to enhance the removal of NMP molecules from the electrode material. Significantly, the resultant MLG OTEs reported free from additional herein are conductive/electroactive components, which allows for their application in spectroelectrochemistry.

## Experimental

#### Chemicals

Natural graphite powder flakes (grade 2369) were supplied by Graphexel Limited (UK). Potassium nitrate (99+%), hexamine-ruthenium (III) chloride [ $Ru(NH_3)_6$ ]Cl<sub>3</sub> (98%), N-

methyl-2-pyrrolidine (NMP) (99+% spectrophotometric grade), 1,2-dichloroethane (DCE) and potassium hexacyanoferrate (II) trihydrate (99%) were purchased from Sigma-Aldrich (UK). Potassium chloride was purchased from Fisher Chemicals (UK). All the solutions were prepared with deionized water (resistivity 18.2 M $\Omega$  cm) from either a PURELAB ultra (Elga, UK) or a Milli-Q (Millipore) system. The polyethylene terephthalate (PET) substrates used were 175 µm thick (HiFi Industrial Film) and the hydrophilic polytetrafluoroethylene (PTFE) filters were of a 0.1 µm pore size (JVWP01300, Millipore Omnipore). Electrodes were contacted using silver conductive paint (Electrolube, supplied by HK Wentworth, UK) and protected with an epoxy overcoat (240-SB from Araldite, UK).

#### **Graphite Exfoliation**

Liquid exfoliation of graphite was carried out using a version of the procedure described by Hernandez *et al.* with NMP as the solvent<sup>30 40</sup>. In a typical synthesis, 0.5 g of powdered graphite was passed through a sieve with a 500  $\mu$ m pore size mesh and added to 100 mL of NMP. The solution was sonicated for 24 hours at 37 kHz, at 40% power, which is equivalent to a true power output of *ca.* 34 W; calculated from the increase in temperature of water under equal sonication conditions <sup>40</sup>. The dispersion was allowed to stand for 12 hours and the large particles were separated by decantation of the NMP. The supernatant was centrifuged at 6000 rpm for 20 min. The concentration of dispersed flakes was calculated using UV-vis absorption spectrometry, using the extinction coefficient (3620 mL mg<sup>-1</sup> m<sup>-1</sup>) reported by the Coleman group<sup>40</sup>, and found to be 0.14 mg mL<sup>-1</sup>. UV-vis absorption indicated that the resulting suspensions were stable for several weeks. This initial concentration of graphene in NMP was used to generate dispersions of in mixed (NMP:DCE) solvents, see below.

#### Electrode Fabrication

To fabricate the films on an insulating substrate we used the following steps: the graphene suspension was mixed with a solvent of lower boiling point; in this report DCE is used. The DCE is added to the NMP/MLG dispersion and made up to a defined volume of NMP and DCE mixture. The two basic parameters used in this study were the total volume of dispersion used to prepare an electrode sample, and the ratio of NMP:DCE in the sample. The various preparation routes are summarised in Table 1 To homogenize, the resulting mixture is sonicated for 5 minutes. Depending on the amount of DCE used, the suspension is stable for 12 to 48 hours. A syringe and a filter holder are used for passing the dispersion through a PTFE filter using manual pressure (see Figure 1). The percolated material on the filter is allowed to dry for a few minutes at room temperature. A PET film is placed over the percolated material creating a three-layer sandwich (the graphene layer is in the middle), which is subsequently placed in a hydraulic press: a weight of 0.5-1.0 tons is applied for 10 minutes. It was found that pressing with weight  $\geq$  3.0 tons damages the film surface, therefore a pressure of 0.5 to 1.0 ton was used over longer periods of time (5-15 min). The percolated MLG film on PET is then allowed to dry for two hours at 75 °C in a vacuum oven (Gallenkamp, UK). Finally, electrical contacts are made with silver paint and a protective epoxy overcoat is applied over the electrical contacts, leaving an average working electrode area of 0.2  $\text{cm}^2$ , a diagram depicting the electrode and its parts is given in Figure 1.

Sample	Figure	Total solvent / mL	NMP:DCE ratio	Mass of graphene / mg	Substrate
1	2 A	Variable	1:4	Variable	Si/SiO <sub>2</sub>
2	2 B	1.5	1:2	0.0700	PET
3	3 A	Variable	1:4	Variable	Si/SiO <sub>2</sub>

**Table 1**. Summary of sample preparation in the work

4	3 B	Variable	1:0	Variable	Si/SiO <sub>2</sub>
-			-		, L
5	4 A	Variable	1:0	Variable	PET
6	4 A and 4 B	1.5	1:4	0.0419	PET
7	5 A	1.5	1:2	0.0719	PET
8	5 A	2.5	1:4	0.0706	PET
9	5A and 7	1.5	1:3.6	0.0151	PET
10	5 A	0.5	1:4	0.0140	PET
11	5 A	0.8	1:4	0.0060	PET
12	5 A	0.5	1:4	0.0040	PET
13	5 B	Variable	Variable	0.3500	PET
14	5 B	Variable	Variable	0.2500	PET
15	5 C	0.5	1:4	0.0095	PET
16	5 C	1.5	1:4	0.0285	PET
17	5 C	2.5	1:4	0.0475	PET
18	6 A	2.5	1:4	0.0705	PET
19	6 A	0.5	1:4	0.0141	PET
20	6 B	2.5	1:4	0.0693	PET
21	6 B	1.0	1:1	0.0693	PET
22	Table 2	3.5	1:4	0.0085	PET
23	Table 2	0.75	1:4	0.0198	PET
24	Table 2	1.0	1:4.2	0.0249	PET



**Figure 1.** Diagram depicting the main steps in OTE fabrication. The inset shows an image of the electrode and its respective parts

### Characterization

Raman spectra were recorded using a Renishaw RM MkI 1000 spectrometer with a 633 nm HeNe laser at power <1 mW and an Olympus BH-2 microscope (50x objective), giving a probe size of 10  $\mu$ m. Atomic force microscopy (AFM) was recorded with a Bruker Multimode 5 Atomic Force Microscope using silicon tips on a silicon nitride lever. Peak force tapping mode with "Scanasyst" was used. Images were analyzed using NanoScope Analysis 1.5 software. Scanning electron microscopy (SEM) was used to obtain images of the deposited films (Philips XL30 SEM). X-ray photoelectron spectroscopy (XPS) measurements were performed on a K-Alpha spectrometer (Thermo Scientific), using a micro-focused monochromatic Al K $\alpha$  source with a spot size of 50  $\mu$ m in 5  $\mu$ m steps. Spectra were analyzed with CASA XPS

software version 2.3.15 and fitted to graphitic carbon using a Shirley background and appropriate relative sensitivity factors.

#### Electrochemistry

Cyclic voltammetry (CV) was performed using an Autolab PGSTAT 100 (Metrohm-Autolab BV, The Netherlands). A single compartment electrochemical cell with three electrodes was used. Platinum ribbon and Ag/AgCl wire (Advent Research Materials, UK) were made in-house and used as counter and reference electrodes, respectively. The sheet resistance of the MLG working electrode was measured using two techniques, namely the four-probe method and the Van der Pauw method<sup>41</sup>. The fourprobe method was carried out in a Jandel four-point meter (Model RM3) with 1.591 mm probe spacing. The sheet resistance was obtained *via* the Van der Pauw method through the Autolab potentiostat and a V&A multimeter (model MY-60). The potentiostat was used to apply a constant current of 5 mA, whilst a current of 1 mA was applied for the thinnest samples. The voltage was recorded using the multimeter.

Spectroelectrochemical measurements were performed at room temperature, using an AUTOLAB PGSTAT 10 potentiostat coupled with a QE65000 Spectrometer (Ocean Optics) made up of a 1044×64 element diode array. The light beam, supplied by a deuterium-halogen light source (Avalight-DH-S, Avantes), was conducted to the spectroelectrochemical cell by 200 µm diameter optical fibres (Ocean Optics BV, Duiven, the Netherlands) and from the cell to the detector by a reflection probe with six 200 µm fibres (Ocean Optics). The spectroelectrochemical cell was designed in house. A three-electrode cell was employed for the spectroelectrochemical measurements, using the transferred MLG OTE as working electrode, a platinum wire as counter electrode and an Ag/AgCl/3M KCl reference electrode, made in house.

# **Results and Discussion**

#### **Graphene and Electrode Characterization**

The flakes were physically characterized using AFM, with the flakes spread on  $Si/SiO_2$ wafers by drop coating and placed in a vacuum oven overnight at 250 °C in order to evaporate the solvent. The distribution of flakes observed using AFM, Figure 2A, are in general agreement with the original work reported by Coleman and co-workers<sup>30</sup>. The majority of the flakes were found to have lateral dimensions ca. 60-80 nm in width, and the flake heights, which were recorded without correction for tip effects, were found on average to be 7 (±1) nm. Note that some larger aggregates (flakes stacked together) were also observed, with lateral dimensions as large as 325 nm and up to 36 nm in height, which is expected from drop-coated samples as a degree of restacking is inevitable. The morphology of the percolated electrodes was investigated using SEM and Raman spectroscopy. Figure 2B shows a SEM image of a percolated MLG electrode surface (i.e. following filtration and transfer to the PET substrate), where the flakes can be seen to be randomly stacked with some of the flake edges detached from the electrode. These features are consistent with previously reported electrodes based on MLG by liquid exfoliation<sup>28</sup>, and the small size of the flakes is due to prolonged sonication during the exfoliation process<sup>42</sup>.



**Figure 2.** (A) AFM image of graphene flakes drop-coated onto a Si/SiO<sub>2</sub> substrate. (B) Representative SEM image of a MLG electrode surface. For preparation conditions see Table 1, sample 1 for AFM and sample 2 for SEM.

Raman spectroscopy performed on the fabricated OTEs also confirmed the film to be composed of few-layer to multi-layer graphene. Spectra consistent with bilayer and trilayer graphene were measured intermittently with those of multi-layer flakes (number of layers <10); a representative spectrum is presented in Figure 3A. The 2D bands in bilayer cases (Figure 3B) fitted well to four Lorentzian functions at 2588 cm<sup>-1</sup> (FWHM =  $50 \text{ cm}^{-1}$ ), 2642 cm<sup>-1</sup> (FWHM =  $52 \text{ cm}^{-1}$ ), 2668 cm<sup>-1</sup> (FWHM =  $40 \text{ cm}^{-1}$ ) and 2694 cm<sup>-1</sup> (FWHM = 41 cm<sup>-1</sup>), which is reasonable for a film sample prepared *via* filtration and compression. 2D bands consistent with monolayer graphene (fitted by a single Lorentzian function) were not observed, although the production of monolayer flakes via the exfoliation method has been reported previously<sup>30</sup>. This could be attributed to the subsequent electrode fabrication procedure.



**Figure 3.** (A) Representative Raman spectrum from the electrode surface. (B) The 2D band of a bilayer spectrum fitted with four Lorentzian functions. For preparation conditions see Table 1, sample 3 for figure A and sample 4 for figure B.

XPS was used to examine the chemical composition of the electrodes, with two samples studied: one prepared with the use of DCE during filtration and one without. Both samples were prepared on PET substrates and were dried for two hours at 75 °C in a vacuum oven. Figure 4A shows the survey spectra of the percolated films with the sample filtered without DCE (sample 5 in Table 1) clearly showing a significant peak at 400 eV, which indicates the presence of residual nitrogen the NMP. Using the N 1s intensities, the concentration of nitrogen was estimated, with the samples filtered with and without DCE having concentrations of 0.57 and 1.92 atom% respectively; the latter being consistent with other reports in the literature<sup>30 43</sup>. The difference is considerable and indicates that the use of DCE during the transfer step can result in the removal of ca. 70% of the nitrogen trapped in the material. As a consequence the residual NMP content in the sample is estimated as 4.5 wt%, which is an improvement on existing reports in the literature<sup>30</sup> (see Supplementary Information for further details). The Thermogravimetric analysis (also see Supplementary Information) confirms this since the weight of loss attributed to the NMP is approximately 4%. This result is important as previous attempts to remove NMP using heat treatments have proved unsuccessful<sup>30,</sup> 43

Figure 4B shows the C 1s XPS spectrum of the sample filtered with DCE (sample 6 in Table 1). The spectrum was de-convoluted into five components: C-C (graphitic) 284.6 eV, C-H 285.5 eV, C-N 285.9 eV, C=O 286.9 eV and COOH (trace amount of oxidised material) 288.8 eV. All the spectra measured were fitted to the graphitic carbon peak with the resultant higher binding energy features being reasonably fitted to the carbon

atoms of NMP and a trace amount of oxidised material. The NMP signals were found to fit well with an approximate intensity ratio of 2:2:1 ((C-H):(C-N):(C=O)), which is expected for NMP. The presence of O 1s (~12.5 atom% for both samples) suggests a considerable percentage of oxygen in the sample, which is assumed to be derived from air since the sample does not receive heat treatment to eliminate the atmospheric adsorbates. Only a trace amount of CI was found in the samples (CI 2p < 0.001 atom%), reflecting the relative volatility of DCE compared to NMP.



(B)



**Figure 4.** (A) XPS survey spectra of a film filtered using fourfold DCE excess for each NMP/MLG dispersion (top, red) and of a film filtered without DCE sample 5 in Table 1 (bottom, black). (B) C 1s XPS spectrum of the sample filtered with DCE, sample 6 in Table 1.

#### **Electrical and Optical Characterization**

The electrical, optical and electrochemical properties of the MLG electrodes were studied by varying the concentration, volume and ratio of the NMP-graphene:DCE mixture used during the graphene-PET transfer. The optical transparency of the electrodes was evaluated by transmittance measurement at 550 nm. Figure 5A shows the plot of transmittance against the sheet resistance of the electrodes, which were fabricated from the graphene suspension and transferred with DCE to give samples denoted 7 to 12 in Table 1. The highest transmittance was observed for electrodes made with the least amount of graphene, which consequently results in higher resistance. These results agree with those previously reported for carbonaceous electrodes since the film thickness plays a crucial role. These values are not acceptable in meeting the requirements of transparent electrode as replacement for

transparent oxides in display applications <sup>44</sup>, however the electrodes at 65% transmittance with a sheet resistance < 70 k $\Omega$  sq<sup>-1</sup> compete with annealed rGO electrodes as reported by Liu *et al.*<sup>45</sup> and Eda *et al.*<sup>8</sup> Methods that involve an annealing process have increased fabrication costs and therefore the approach proposed herein has the advantage of being more affordable and also uses a flexible substrate.

The effect of the DCE volume used during transfer was also studied: it was observed that the ratio of volume of graphene suspension (in NMP) and volume of added DCE influences the sheet resistance, which is defined as a ratio of DC resistivity to film thickness, and the electrochemical properties. This effect was studied in thicker films and Figure 5B shows that when a larger total graphene mass (sample 13 in Table 1) was transferred the sheet resistance,  $R_s$ , decreased as the volume of DCE increases: similar behaviour was also observed when a lower mass of graphene was transferred (sample 14 in Table 1). These results confirm that the DCE molecules are displacing residual NMP molecules between the individual graphene layers, and lead to reaggregation of the material (as the more volatile DCE evaporates) hence increasing its conductivity.

The Van der Pauw method was used to corroborate the sheet resistance of the samples with 1:4 NMP:DCE ratio. Two vertical resistances and two horizontal resistances were obtained for each sample and the Van der Pauw equation<sup>41</sup> was used to estimate the sheet resistance (see Supplementary Information). Figure 5C shows the sheet resistances of electrodes made with different volumes of suspension, specifically samples 15 (100µL:  $3.07 (\pm 1.33) \times 10^3 \Omega \text{ sq}^{-1}$ ), 16 ( $300\mu$ L:  $1.35 (\pm 0.28) \times 10^3 \Omega \text{ sq}^{-1}$ ) and 17 ( $500\mu$ L:  $795 (\pm 175) \Omega \text{ sq}^{-1}$ ) of MLG dispersion, revealing the trend in resistance as a function of the mass of graphene added. Again, the sample numbering is defined in Table 1.





(A)



**Figure 5.** (A) Transmittance at 550 nm plotted *vs* sheet resistance for electrodes fabricated from the initial graphene suspension in NMP and transferred with varying amounts of DCE. Data corresponding to samples 7 to 12 are indicated in the Table 1. (B) Estimated sheet resistance with respect to the mole fraction,  $\chi_{DCE}$  used during filtration. Samples with 0.35 mg (black points) and 0.25 mg (red points) of graphene transferred, samples labelled as 13 and 14 in Table 1. (C) Sheet resistances of the films measured using the Van der Pauw method for electrodes made with 100 µL, 300 µL and 500 µL MLG dispersions (i.e. samples 15-17); the samples were transferred onto PET using an NMP:DCE ratio of 1:4. See samples 15 to 17 in Table 1 for detail on composition..

#### **Electrochemical Characterization**

Electrochemical characterization was performed using hexacyanoferrate (II) as a model redox couple, with cyclic voltammetry and chronoamperometry, in a 1 to 3 mM  $K_4$ [Fe(CN)<sub>6</sub>] solution using 1 M KNO<sub>3</sub> as supporting electrolyte. The amount of transferred graphene also affects the electrochemical behavior. Figure 6A shows cyclic

voltammograms obtained for two electrodes fabricated from 100  $\mu$ L and 500  $\mu$ L volume graphene solutions (labelled as 18 and 19 in Table 1), respectively. The electrode with the lower amount of graphene, 100  $\mu$ L (sample 18), shows a large peak separation due to the higher resistance of the material, which can be attributed to a sparser percolating network of graphene. The effect of the NMP:DCE ratio is shown in Figure 6B, for a constant amount of graphene used, and for varying volumes of DCE during the filtration. It is noted that the position of the oxidation and reduction peak are close in both cases, however, the background current is lower when the NMP:DCE ratio is 1:4 (sample 20 in Table 1). Otherwise, a well-defined voltammogram is recorded when volume of DCE is increased. This may be due to slow evaporation of NMP, which does not permit the adequate transfer of graphene onto PET film. However a greater volume of DCE is not recommended, as this increases the apparent resistance of the sample.





**Figure 6.** (A) Cyclic voltammograms recorded for two electrodes using different volumes of graphene solution during filtration: sample 18 (red line), sample 19 (black line). Measuring solution: 3 mM hexacyanoferrate (II)/ (III) in 1 M KNO<sub>3</sub> at 10 mV/s. (B) CVs for two electrodes prepared with different NMP:DCE ratios. In black, electrode made with a NMP:DCE ratio of 1:4 (sample 20 in Table 1). In red, electrode made with a NMP:DCE ratio of 1:1 (sample 21 in Table 1). Measuring solution: 3 mM potassium hexacyanoferrate in 1 M KNO<sub>3</sub> at 200 mV/s.

Samples with mass between 0.0151 and 0.0285 mg and 1:4 /NMP:DCE ratio yielded sheet resistances below 2 k $\Omega$  sq<sup>-1</sup> and a linear relationship between current and the square root of voltage scan rate was obtained, indicating that the charge transfer process in these cases occurred under diffusive control. However, the voltammetric response in other cases (with lower amounts of transferred graphene) showed more distortion, which is indicative of the resistance arising from the electrodes, the sheet resistance,  $R_S$ , measured for each of the electrodes are given in Table 2. For example, the voltammetric peak separations,  $\Delta E_p$ , were as high as 731 mV, at 0.1 V s<sup>-1</sup>, for electrodes with ~65 % transmittance.

**Table 2.** Sheet resistances measured for percolated electrodes prepared with using aconstant NMP:DCE ratio of 1:4.  $R_s$  were measured using the van der Pauw method.

Electrode	Sample 12	Sample 22	Sample 23	Sample 24
$R_s / \Omega sq^{-1}$	69152	10066	1634	1488

It is relevant to note that peak separation and sheet resistance data are not as low as those previously reported for graphene based electrodes<sup>19, 28, 31</sup>, however the important distinction here is that the previously reported electrochemical data was obtained using modified glassy carbon electrodes or other conductive substrates. In this study, the substrate is a non-conductive material, and therefore the electrical and electrochemical response can only be attributed to the dispersed graphene material.

### Spectroelectrochemistry

The graphene OTEs fabricated from 300  $\mu$ L of graphene solution (Sample 9 in Table 1) have transmittance values comparable to current OTEs used in spectroelectrochemistry<sup>46</sup>. In order to verify their suitability as electrodes in measurements designed to follow electrochemical reactions through visible spectra,  $K_4$ [Fe(CN)<sub>6</sub>] was again used as the model redox system. In fact this compound is routinely used as a standard chemical system for spectroelectrochemistry<sup>46</sup>, to test the performance of the OTEs.

Cyclic voltammetry between potential limits of -0.2 V and 0.7 V at a scan rate of 0.01 V s<sup>-1</sup> was performed in a 1 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution that contains 1 M KNO<sub>3</sub> as supporting electrolyte. Figure 7 shows the full spectra recorded during the experiment, with the inset showing the corresponding cyclic voltammogram. As expected, the

appearance of the characteristic absorption band of  $[Fe(CN)_6]^{3-}$ , centred at 420 nm, was observed on its generation from the electro-oxidation of the colourless  $[Fe(CN)_6]^{4-}$ . Absorbance increases at 420 nm during the anodic scan and decreases during the cathodic one, concomitantly with the cathodic peak observed in the voltammogram. Therefore, we can affirm that graphene OTEs show both reasonable electrochemical and spectroscopic signals, demonstrating that these electrodes are well suited to study electrochemical processes using spectroelectrochemistry.



**Figure 7.** 3D absorbance/time (potential)/wavelength plot obtained during the potential scan in a 1 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution containing 1 M KNO<sub>3</sub> as supporting electrolyte. Potential was scanned at 0.010 V s<sup>-1</sup> from -0.20 V to 0.70 V. Inset: the corresponding cyclic voltammogram. Data was taken with sample 9 in Table 1.

## Conclusions

Graphene OTEs supported on a transparent and flexible PET substrate have been fabricated using a simple methodology that minimises the trapped solvent content. The graphene flakes were prepared *via* an existing method involving the liquid-phase exfoliation of graphite, which produces metastable dispersions of monolayer to multi-layer flakes in NMP. The transfer technique developed uses a low boiling point solvent, DCE, for partial solvent exchange with the less volatile NMP, and XPS data suggests that the exchange results in a considerable improvement on existing techniques in producing solvent free graphene-based OTEs, furthering the NMP removal by a 70% without the need for annealing.

The physical characterisation is supported by electrochemical studies, which allowed for the optimisation of the transfer process. Electrodes with increased conductivities are produced as the amount of graphene transferred increases, and larger DCE volumes with respect to NMP produces electrodes of lower resistance; optimal at a 1:4 NMP:DCE ratio. The latter finding indicates that intercalating NMP molecules are replaced by DCE, which being more volatile, leads to the enhancement of the OTE electrical properties. Crucially, the OTEs have been shown to demonstrate an effective electrochemical response and although the transmittance values are relatively low, graphene-based electrodes sufficiently transparent these are for spectroelectrochemical studies.

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