1. Introduction

One of the many advantages of carbon as electrode material is its relatively inert electrochemistry. However, carbon has a rich surface chemistry, and while this property is useful in that it allows the chemical modification of the electrode surface, it can also lead to unwanted oxidation in the presence of atmospheric oxygen and moisture [1,2]. The interaction of various redox species with oxygen functionalities at carbon electrodes has been investigated extensively by McCready and coworkers [3–5]. Common redox probes can be classified roughly into three categories: those which are insensitive to surface termination (FeMeOH, [Ru(NH₃)₆]³⁺/²⁺); those which interact with specific oxygen functionalities (such as Fe³⁺/²⁺ with C=O) and those which are surface sensitive but apparently do not interact with specific oxygen-containing groups ([Fe(CN)₆]³⁻/⁴⁻) [1].

As higher surface area nanomaterials are used, the role of carbon surface chemistry becomes increasingly important. In the past decade since it was first studied experimentally [6], graphene has attracted enormous interest in electrochemical applications owing to its large surface area and remarkable electronic properties [7–14]. Pristine graphene manufactured via mechanical exfoliation cannot be produced in bulk quantities. As graphene is increasingly being manufactured via reduction of graphene oxide, where an array of oxygen groups persist in the final product, the interaction of oxygen moieties with solution species will have an influence on the electrochemical response. The large variety of possible oxygen functionalities at the electrode surface makes it difficult to attribute changes in electrochemical response to specific functional groups.

Our approach to studying the influence of oxygen functionalities on the electrochemical response of graphene is to use novel graphene nanoflakes (GNF). GNF have average lateral dimensions of just 30 nm, confirmed by AFM imaging [15] with a graphene basal plane that is largely defect free. The edges of the GNF are decorated with carboxylic acid (COOH) groups, as shown by XPS and ATR-FTIR [15]. The high-resolution XPS spectrum of the C₁s region can be fit with two peaks: a main peak at ca. 285 eV corresponding to sp² carbon and a second peak at ca. 289 eV assigned to the presence of COOH edge groups. There is no evidence for the presence of sp² carbon bonding, or oxygen functionalities other than COOH. Likewise, the ATR-FTIR spectrum shows a strong v(C=O) peak at 1717 cm⁻¹, which is consistent with a carboxylic acid functionality and in good agreement with XPS data. Thus these GNF allow us to study the influence of the COOH groups on...
...electrochemical reaction in isolation, as there are no other oxygen functionalities present. Additionally, these edge groups are present in high density and the small size of the GNF means their influence on the electrochemical performance of the flakes will be amplified.

The results presented in this paper concern the influence of the COOH edge group on the redox response of the $[\text{Fe(CN)}_6]^{3-/4-}$ couple and follow from previously reported results from our group [16]. When this redox couple was investigated using an electrode modified with COOH-terminated GNF, its voltammetric response was found to become highly irreversible as the solution pH was decreased below pH 8. At low solution pH (<6) and ionic strength the cyclic voltammetric (CV) response was very inhibited and sigmoidal in form, consistent with presence of an adsorbed blocking species at the electrode surface. When GNF terminated with amide functionalities were used instead, they were found to have no noticeable effect on this redox reaction, indicating that the COOH edge groups are responsible for the observed inhibition. Other redox probes, such as ferrocene methanol, were found to be insensitive to the identity of the GNF edge groups, so it was clear that the $[\text{Fe(CN)}_6]^{3-/4-}$ species in particular was affected by the COOH groups. Previous studies [1,4,5] have found the ET kinetics of this reaction to become slower with increasing, rather than decreasing, pH, and attributed the effect to electrostatic repulsion between charged redox probe. In the case of COOH-GNF modified electrode, pH was manipulated by subtracting a spectrum of COOH species in particular was affected by the COOH edge groups. From the titration data the number of acidic protons appeared that the stability and reversibility of electron transfer occurred over a wide pH range of ca. pH 3–8. This behaviour was attributed to different bonding environments or electrostatic/hydrogen-bonding interactions between neighbouring COOH groups.

2. Experimental

2.1. Chemicals

The GNF were prepared from multiwalled carbon nanotubes (5–20 nm outer diameter and 2–6 nm inner diameter) by chemical oxidation as reported previously [15] with some modification to the method to allow for scale-up. All other chemicals were purchased from Sigma–Aldrich and used as received. All H$_2$O solutions were prepared using water from a Milli-Q water purification system, with a resistivity of not less than 18.2 MΩ cm at 25 °C.

2.2. Cyclic voltammetry and electrode preparation

The experimental procedure has been reported previously [16]. CV experiments were carried out using a µ-Autolab potentiostat (Eco Chemie, NL) running GPES (v4.9) software. A boron-doped diamond (BDD) disk, 3 mm in diameter and sealed in PEEK (Windsor Scientific) was used as the working electrode, either unmodified or modified with a layer of adsorbed GNF. A coiled platinum wire served as a counter electrode. The reference electrode was Ag/AgCl (sat. KCl) (BASI, US) and all potentials are reported relative to it. The BDD electrode was polished using successively finer grades of alumina suspension down to 0.05 μm, rinsed thoroughly with ultrapure water and dried using an ambient air flow. For experiments using GNF-modified electrodes, GNF samples were drop-cast from aqueous suspensions of known concentration onto the freshly polished BDD electrode using a micropipette and allowed to dry under ambient conditions. After drying, the electrode was rinsed thoroughly with ultrapure water to remove any poorly adhered material from the surface and dried using an ambient air flow. The resulting amount of GNF on the electrode was estimated at 1.5 ± 0.5 μg in all experiments, and all CVs were recorded using a freshly modified electrode. In other experiments a known concentration of GNF was simply added to the solution along with the redox probe.

2.3. Solution-phase ATR-FTIR

2.3.1. Characterisation of GNF

Solution-phase characterisation of GNF was performed by recording mid-infrared spectra in attenuated total reflectance (ATR) mode with a Bruker Tensor 27 spectrometer (Bruker, United Kingdom) fitted with a room temperature DLaTGS detector at 4 cm$^{-1}$ resolution and a diamond crystal as the internal reflection element. A droplet (volume ca. 50 μl) of an aqueous suspension of the GNF was applied directly onto the ATR crystal and the sample was introduced at one end via a syringe. Spectra recorded in H$_2$O and D$_2$O were manipulated using the baseline and atmospheric compensation function of OPUS software. Changes in concentration due to the addition of aqueous aliquots of base were compensated by multiplying the spectra by the volume ratio.

2.3.2. $[\text{Fe(CN)}_6]^{3-/4-}$ stability experiments

The stability of $[\text{Fe(CN)}_6]^{3-/4-}$ in solution was investigated by recording the IR absorption of the cyanide ligands over a 24-h period. A stainless steel cell was placed on top of the IRE with two narrow steel tubes at the top of the cell that acted as the inlet and outlet for the sample. Plastic tubing was attached to the steel tubes and the IRE was introduced at one end via a syringe. The sample was then pumped back and forth to remove any air bubbles. The length of the plastic tubing and the small surface area exposed to the atmosphere meant that contamination of samples in D$_2$O by atmospheric water was minimised. A single spectrum was computed by Fourier transformation of 250 averaged interferograms for background and sample and the software was programmed to record a spectrum every 60 min. The background spectrum was of pure water and air for experiments in H$_2$O and D$_2$O, respectively. Spectra recorded in H$_2$O were manipulated using the baseline and atmospheric correction functions in OPUS software. Spectra recorded in D$_2$O were manipulated by subtracting a spectrum of D$_2$O only, which was first scaled to match the absorbance at 2080–2740 cm$^{-1}$ in sample spectra.

2.4. Spectroelectrochemical experiments

To probe the effect of solution-phase GNF on the reversibility of the $[\text{Fe(CN)}_6]^{3-/4-}$ redox couple, the IR absorption of the cyanide ligands was monitored during oxidation and reduction using an in-situ technique. ATR-FTIR spectra were recorded with a Bruker IFS 66/S spectrometer (Bruker, United Kingdom) fitted with a liquid nitrogen-cooled MCT-A detector and a silicon ATR prism at 4 cm$^{-1}$ resolution. An electrochemical cell with a volume of 20 μl was used with a Pt mesh working electrode situated 0.1–0.3 mm
above the prism. A Pt sheet counter and Ag/AgCl reference electrode were placed in a chamber separated from the sample chamber by a Vycor frit. Working electrode potentials were set at 0 V for reduction of [Fe(CN)₆]³⁻ to [Fe(CN)₆]⁴⁻ and +350 mV for oxidation of [Fe(CN)₆]⁴⁻ to [Fe(CN)₆]³⁻. IR difference spectra were constructed by recording a background spectrum at one potential, then switching to the second potential and recording a sample spectrum at specific time intervals.

3. Results

3.1. ATR-FTIR characterisation of GNF in solution

The solution-phase IR spectra of solvated GNF are shown in Fig. 1. Initially, when only water and GNF are present and no base has been added, the pH of the solution is approximately 2 as determined with pH indicator paper. Absorption bands can be seen at 1720 cm⁻¹ (C=O stretch), 1590 cm⁻¹ (asymmetric COO⁻ stretch), 1420 cm⁻¹ (symmetric COO⁻ stretch) and 1260 cm⁻¹ (overlapping C–O stretch and O–H deformation). The GNF are partially deprotonated already before the addition of base, as indicated by the low pH of the solution and the peaks corresponding to both protonated and deprotonated forms of COOH. Adding increasing aliquots of KOH causes the signal from the C=O and C–O stretches associated with protonated carboxylic acid to decrease, whereas the two bands from COO⁻ gain intensity with added base. Changes can also be observed in the O–H stretch region where a decrease in absorption intensity is seen around 3290 cm⁻¹ and increase around 3300 cm⁻¹. Because a background spectrum of pure water was recorded, the O–H stretch of water is subtracted from the sample spectra which initially leads to a negative feature centred at 3300 cm⁻¹. The increase in absorption at 3300 cm⁻¹ upon addition of base is assigned to increased solvation of the deprotonated carboxylate groups. At the same time, the intensity of absorption around 2700 cm⁻¹ decreases and this is attributed to the loss of hydrogen-bonded COOH groups. The final spectrum in Fig. 1 is recorded at pH ca. 7. Thus these in situ pH studies agree with our former observations that the flakes occupy a range of protonation states in solutions of pH 3–7.

3.2. Cyclic voltammetric studies of [Fe(CN)₆]³⁻/⁴⁻ redox couple in the presence of GNF

To explore further our previous observations [16] that the [Fe(CN)₆]³⁻/⁴⁻ species are unstable in the solution environment surrounding the GNF, cyclic voltammetry was performed with both [Fe(CN)₆]³⁻ and GNF present in solution. All CVs were recorded at a freshly polished, clean BDD electrode. The experiment was also carried out with the [Ru(CN)₆]³⁻/⁴⁻ redox species in solution for comparison. It can be seen from Fig. 2 that presence of GNF in solution influences both redox reactions, but the extent to which this happens differs greatly. In the case of [Fe(CN)₆]³⁻/⁴⁻, the presence of GNF in solution leads to a small increase in peak separation and a small decrease in peak height. In the case of [Fe(CN)₆]³⁻/⁴⁻, on the other hand, the peak height is drastically reduced and the voltammogram has a sigmoidal shape, indicative of electrode blocking. This is the same response as we obtained when COOH-terminated GNF were immobilised directly on the electrode surface [16]. The decrease in current observed for the [Ru(CN)₆]³⁻/⁴⁻ couple we attribute to a small lowering of the effective diffusion coefficient of the probe due to the large GNF particles dispersed in the solution. We would expect a similar inhibition for [Fe(CN)₆]³⁻/⁴⁻; however these results indicate that GNF have a profound effect on the electron transfer process of this species, rather than simply blocking diffusion. As we reported previously [16] it is specifically the COOH edge groups which affect the [Fe(CN)₆]³⁻/⁴⁻ in this way, suggesting a protonation process may be responsible for these observations.

Having established the importance of the acidic functionalities in electron transfer process for [Fe(CN)₆]³⁻/⁴⁻ CV experiments were carried out in low ionic strength (0.01 M KCl) solutions with GNF immobilised on the electrode surface and either H₂O or D₂O as the solvent. The results are presented in Fig. 3. When H₂O is used as the solvent, the CV shows significant inhibition in the first cycle. The response improves slightly during repeated cycling, but the 10th cycle still shows significant irreversibility of the redox reaction. In D₂O, the first cycle shows inhibited electron transfer, but the response improves during repeated cycling with increase in peak heights and decrease in peak separation. By the tenth scan, the response in D₂O is essentially reversible.

![Fig. 1. Changes in IR absorption of GNF upon addition of 0.1 M KOH. GNF with no added base at pH 2 (black), pH 3 (red), pH 5 (green), pH 7 (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 2. CVs of GNF only (black): 0.5 mM [Fe(CN)₆]³⁻ (dashed blue); 0.5 mM [Fe(CN)₆]³⁻ and 34 µg ml⁻¹ GNF (solid blue); 0.5 mM [Ru(CN)₆]³⁻ (dashed red); 0.5 mM [Ru(CN)₆]³⁻ and 34 µg ml⁻¹ GNF (solid red). Electrolyte: 0.01 M KCl. Scan rate: 50 mV s⁻¹. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image2)
When the GNF are surrounded with H₂O molecules, the constant protonation and deprotonation of the carboxylic acid edge groups does not lead to a change in the chemical identity of the acid groups. However, if the H₂O molecules are replaced by D₂O, the dynamic acid–base equilibrium will gradually lead to predominately COOD around the flake edges as the protons are exchanged and diffuse away from the electrode surface. Therefore we propose that during the first cycles in D₂O, the GNF edges are still mostly decorated with COOH groups and these inhibit the redox reaction. However, as COOD groups begin to dominate, the redox reaction is allowed to proceed uninhibited, leading to a near reversible CV by the 10th scan. The results also suggest that if an electrode blocking species is responsible for the inhibited electron transfer, it forms reversibly and can dissolve or desorb from the electrode surface according to changes in the diffusion layer. Thus the redox reaction is able to become more reversible with cycling in D₂O as the concentration of protons at the GNF-modified electrode surface decreases.

3.3. Spectroelectrochemistry of [Fe(CN)₆]³⁻/⁴⁻

The [Fe(CN)₆]³⁻/⁴⁻ redox reaction can be conveniently monitored with ATR-FTIR because the cyanide stretch is sensitive to the oxidation state of the iron centre. [Fe(CN)₆]³⁻ absorbs at 2116 cm⁻¹, whereas in [Fe(CN)₆]⁴⁻ the absorption frequency is shifted to 2036 cm⁻¹ and the extinction coefficient is four times larger. ATR-FTIR coupled with in-situ controlled potential experiments were performed for 1 mM K₃[Fe(CN)₆] in 0.01 M KCl. The sample was introduced to the in situ electrochemical cell and a potential of 0 V was applied to drive the reduction of [Fe(CN)₆]³⁻ to [Fe(CN)₆]⁴⁻. The resulting IR spectrum shows a negative [Fe(CN)₆]⁴⁻ band and positive [Fe(CN)₆]³⁻ band (solid line, Fig. 4a). When the intensity of the [Fe(CN)₆]⁴⁻ band did not increase anymore, all [Fe(CN)₆]³⁻ present in the sample chamber was assumed to have been converted to [Fe(CN)₆]⁴⁻. The reaction reached completion in about 2 min, as indicated by the intensity of the [Fe(CN)₆]⁴⁻ band. The height of the [Fe(CN)₆]⁴⁻ band as a function of time is plotted in Fig. 4b. The potential was then switched to +350 mV to oxidise [Fe(CN)₆]⁴⁻ back to [Fe(CN)₆]³⁻. The resulting IR spectrum shows a positive [Fe(CN)₆]⁴⁻ band and negative [Fe(CN)₆]³⁻ band (dashed line, Fig. 4a). As was the case for the reduction, the negative [Fe(CN)₆]⁴⁻ band reached full height after about 2 min, indicating full conversion back to [Fe(CN)₆]³⁻.

The [Fe(CN)₆]³⁻ solution was then replaced by a solution containing 1 mM K₃[Fe(CN)₆] in 0.01 M KCl and 3.2 µg ml⁻¹ of GNF. The concentration of acidic protons from the GNF is estimated to be 22 µM and only a small fraction would be dissociated. Therefore the GNF did not significantly alter the pH of the solution. The experiment was then repeated and a potential of 0 V applied. With the GNF present, the reaction proceeded much more slowly. After 2 min, the [Fe(CN)₆]⁴⁻ band was only 40% of the intensity expected for full conversion of [Fe(CN)₆]³⁻ to [Fe(CN)₆]⁴⁻. Full conversion took approximately 9 min, compared to 2 min for the same volume and concentration of the control solution. The influence of GNF on the oxidation reaction was essentially the same.

The observations reported here support the CV experiments described in Section 3.2. The presence of GNF clearly inhibits the reversibility of the [Fe(CN)₆]³⁻/⁴⁻ redox couple. Moreover, it was shown in Fig. 2 that the observed decrease in current could not be explained by diffusion effects alone. Therefore, the reason why the reaction takes longer to complete with GNF in solution is likely to lie in the solution stability of the redox species.

3.4. Monitoring the stability of [Fe(CN)₆]³⁻/⁴⁻ with ATR-FTIR

Berier and Fletcher [17] made the observation that the poisoning of an electrode surface by the [Fe(CN)₆]³⁻/⁴⁻ redox couple required the presence of both Fe(II) and Fe(III) species. We therefore used an equimolar solution of K₃[Fe(CN)₆] and K₄[Fe(CN)₆] in H₂O to probe their stability in solution in the absence of applied potential. To gauge the impact of GNF on the stability of [Fe(CN)₆]³⁻/⁴⁻, a second solution was prepared, this one also containing 30 µg ml⁻¹ GNF. The concentration of GNF was high enough to impart a brownish hue to the solution but low enough to not alter the pH significantly (pH of both solutions 6.5 ± 0.1).

The IR spectrum of both samples initially shows two peaks; the [Fe(CN)₆]³⁻ CN stretch at 2036 cm⁻¹ and the [Fe(CN)₆]⁴⁻ CN stretch at 2116 cm⁻¹ (Fig. 5). No peaks are detected in the 1700–1200 cm⁻¹ region that could be associated with GNF, although the concentration of flakes is too low for this purpose. Over time, a third peak begins to emerge in both samples. In the control solution, this peak at 2069 cm⁻¹ is detectable above the noise after about 13 h, whereas with GNF in solution, the intensity of this third peak surpasses that of the [Fe(CN)₆]³⁻ peak after 3 h. Mixing the GNF sample by pumping gently with a syringe back and forth caused a decrease in the intensity of the peak at 2069 cm⁻¹. The new band is very high in intensity compared to the other two CN stretch bands. Given that the [Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ bands are not greatly diminished, it is clear that the new cyano species cannot be present in high concentration. The intensity of the new band may then be due to either a species present in low concentration with a high extinction coefficient, or the accumulation of a species in the region near the ATR prism. A new species
with a high extinction coefficient is unlikely, as the most plausible solution species candidate that absorbs in this region is free cyanide, the absorption coefficient of which is very small compared to the bound form [18]. The most likely explanation is the accumulation of a non-soluble species at the surface of the internal reflection element, which in the cell geometry is at the bottom of the cell. This would also explain why the intensity of the other CN stretch bands does not change significantly, since the amount of precipitate does not need to be large in order to give an appreciable signal. UV–Vis spectra taken in situ with the same solution (not shown) do not offer evidence of the formation of a coloured species, but it is important to bear in mind that the UV–Vis probes the bulk solution (where the overall concentration of this new species is low) whereas ATR-FTIR only reaches a few microns at the bottom of the cell (where the species accumulates).

As described in Section 3.2, the identity of solvent has a marked influence on the reversibility of the [Fe(CN)]₃³⁻/⁴⁺ redox couple. To further explore this, stability experiments were repeated in D₂O as shown in Fig. 6. In H₂O, a new band appeared in between the two cyanide stretch bands after a couple of hours. In D₂O, no new band is seen after four hours whereas in H₂O the new band at that point was already comparable in size to the [Fe(CN)]₄⁴⁺ stretch. After 24 h in D₂O the new band did become evident, but its appearance is accompanied with a H₂O band due to H₂O contamination from atmospheric moisture, leading to the conclusion that the presence of appreciable concentration of protons is necessary for the decomposition/precipitation reaction to proceed.

4. Discussion

Above, we have described how the presence of GNF influences the [Fe(CN)]₃³⁻/⁴⁺ redox system. In our previous work [16] it was determined that it is specifically the acidic groups around the edges of GNF that are responsible for the irreversible behaviour of the [Fe(CN)]₃³⁻/⁴⁺ redox couple. Here, we have explored further the influence of protons on this redox reaction. The reversibility and electron transfer rate of the [Fe(CN)]₃³⁻/⁴⁺ redox system has been shown by others to also depend on the concentration and identity of cations in solution [17,19]. Peter et al. have suggested...
that the rate of electron transfer depends on the concentration of an activated species containing one or more cations, and that electron transfer is considerably lower in the absence of ion-pairing, for example in electrolyte solutions of low ionic strength [19]. Additionally, it is known that [Fe(CN)₆]³⁻/⁴⁻ can be unstable in solution of low ionic strength and low pH, and cyanide ligand loss and subsequent decomposition and adsorption onto electrodes have been observed by several groups [17,20–25]. Protonation and decomposition of [Fe(CN)₆]³⁻ have been observed to occur simultaneously [26], and although our sample solutions at pH 6 would not be considered acidic enough to cause decomposition of [Fe(CN)₆]³⁻, the high density of COOH groups on the GNF may lead to localised acidic conditions, promoted by the ready availability of protons at the edges of the flakes. Thus there are several mechanisms by which the very acidic local environment of the COOH-GNF could inhibit electron transfer, including disruption to the ion-paired activated species required for fast electron transfer, protonation of CN ligands, loss of ligands or formation of insoluble decomposition products.

When deuterated water is substituted for H₂O, the presence of GNF has much less influence on the [Fe(CN)₆]³⁻/⁴⁻ redox reaction. Consecutive cycles in D₂O saw the voltammetric response of [Fe(CN)₆]³⁻/⁴⁻ quickly return to near reversible. ATR IR also showed the [Fe(CN)₆]³⁻/⁴⁻ species to be more stable in the presence of GNF when dissolved in D₂O rather than H₂O. The substitution of deuterium for hydrogen in a water molecule has little effect on the molecular dimensions defined by bond length and bond angle, but the O–D bond is slightly stronger than the O–H bond. The difference in bond strength leads to a smaller dissociation constant for D₂O than H₂O, making H₂O a fivefold stronger acid [27]. Liquid D₂O is more viscous than liquid H₂O and has a slower rate of molecular reorientations and translations [28], leading to the conclusion that there is more structural order in D₂O due to a higher degree of hydrogen bonding [29]. This can be attributed to lower intermolecular vibrational frequencies caused by isotopic substitution but also the greater strength of hydrogen bonding in D₂O than in H₂O [29]. Additionally, protons are able to diffuse rapidly in water via the Grotthuss mechanism [30]. It has recently been demonstrated that the mechanism is strongly influenced by the local hydration structure of the proton and involves the concerted motion of several protons [31]. The reorganisation and rotation of molecules involved in the Grotthuss mechanism are slower in D₂O than in H₂O, making heavy water less efficient in proton transport. Thus the instability of [Fe(CN)₆]³⁻/⁴⁻ in the presence of GNF appears to be exacerbated by the readily available H⁺ in the localised acidic conditions in the region of the carboxylic acid edge groups. Increased stability in D₂O can be attributed either to the increased strength of the O–D bond (making D⁻ less available) or slower diffusion of D⁻ from the GNF to [Fe(CN)₆]³⁻/⁴⁻.

The results described in Section 3.4 lead to the interpretation that the presence of GNF in an aqueous solution of K₃[Fe(CN)₆] and K₄[Fe(CN)₆] promotes the decomposition of [Fe(CN)₆]³⁻/⁴⁻. The intense new IR absorption band that emerges after or during the reduction of [Fe(CN)₆]³⁻/⁴⁻ in the presence of GNF was concluded to be a adsorbed intermediate whose absorption occurred between 2070–2080 cm⁻¹ [32]. ATR-FTIR experiments using the Bruker ISF 66/S spectrometer were performed at the Glynn Laboratory, UCL. The help and advice by Prof Peter R. Rich and his group is gratefully acknowledged.

5. Conclusions and future work

COOH-terminated GNF have been used to probe the influence of acidic functionalities on the [Fe(CN)₆]³⁻/⁴⁻ redox couple by cyclic voltammetry and controlled-potential experiments with in-situ ATR-FTIR. The redox reaction is severely inhibited by the presence of the GNF in solution as well as at the electrode surface, supporting the conclusion that GNF promote instability of [Fe(CN)₆]³⁻/⁴⁻ in solution. The formation of a precipitate from solutions of [Fe(CN)₆]³⁻ and [Fe(CN)₆]⁴⁻ in the presence of GNF was concluded from ATR-FTIR spectroscopy. The precipitate did not form when D₂O was used as the solvent. GNF had much less influence on the redox reaction in D₂O, highlighting the role played by readily available protons at the flake edge.

We have suggested here that the instability of [Fe(CN)₆]³⁻/⁴⁻ may be caused by protonation and subsequent decomposition of the complex anion. Work is under way to monitor this process and the protonation state and H⁺/D⁺ exchange of the carboxylic acid edge groups around GNF dissolved in D₂O with ³H NMR. At a given temperature, D₂O is more structured than H₂O, hence substituting D₂O for H₂O is therefore comparable to lowering the temperature of the solution. Therefore it would be interesting to see if there is a temperature dependence of the CV response of [Fe(CN)₆]³⁻/⁴⁻ in H₂O when GNF are present. Other solvents will also be used to study the influence of GNF on the reversibility and stability of this redox couple.

Understanding the role of different oxygen-containing functional groups on the electrochemical performance of graphene materials is essential in determining the importance of defect chemistry when it is used as an electrode. Here we have been able to study the influence of COOH groups in isolation as our well-characterised flakes are shown to contain no other functionalities. By changing the GNF terminations we aim to study the effect of other edge groups on the electrochemical response of graphene.

Conflict of interest

The authors confirm that there is no conflict of interest.

Acknowledgments

We thank EPSRC/UCL Chemistry Department for studentship for Mailis Lounasvuori and Martin Rosillo-Lopez. Christoph Salzmann thanks the Royal Society for the award of a URF. The work was funded partly by EPSRC grant EP/J010006/1. ATR-FTIR experiments using the Bruker IFS 66/S spectrometer were performed at the Glynn Laboratory, UCL. The help and advice by Prof Peter R. Rich and his group is gratefully acknowledged.

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