On the Role of Transition Metal Salts During Electrochemical Exfoliation of Graphite: Antioxidants or Metal Oxide Decorators for Energy Storage Applications

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A new approach is presented, based on the unexpectedly versatile role of transition metal ions, to produce high-quality graphene via an anodic electrochemical exfoliation route, and the capability of the resultant material in energy storage applications are illustrated. The method is based on graphene exfoliation in the presence of transition metals (Co$^{2+}$ and Fe$^{3+}$) which act as antioxidants, preventing surface oxidation of graphene, while other metals (Ru$^{3+}$, Mn$^{2+}$, Ir$^{3+}$, and Sn$^{4+}$) act as metal oxide decorators. The addition of Co$^{2+}$ ions to the exfoliation solution produced few-layer graphene that is two orders of magnitude more conducting and contains 80% less oxygen than the material obtained in the absence of cobalt ion. By contrast, the use of Mn$^{2+}$ and Ru$^{3+}$ in the electrolyte form an interconnected honeycomb lamellar structure of MnO$_2$ and RuO$_2$ nanoparticles, respectively. The combination of Mn$^{2+}$ and Ru$^{3+}$ create a uniformly grown Ru–Mn oxide hybrid structure on the graphene sheets in a single stage process, which is found to be an efficient electrode for supercapacitors (specific capacitance of 500 F g$^{-1}$) and as a bifunctional water splitting electrocatalyst. The use of these inexpensive salts will aid the scalable production of high-quality graphene and functionalized graphene for diverse applications.

1. Introduction

Since the isolation and characterization of graphene in 2004 by Novoselov et al., a plethora of reports have discussed its unusual properties including its strength, transparency, and ability to conduct both heat and electricity. Owing to these and other unusual properties, graphene is extremely interesting both scientifically and technologically, with many applications being developed which exploit both the mechanical and electronic properties of the material.

Scalable production of high-quality graphene therefore presents itself as a major challenge for researchers. Although a range of techniques including bottom–up (chemical vapor deposition, epitaxial growth from silicon carbide) and top–down (chemical exfoliation, solution exfoliation, or mechanical exfoliation) synthetic approaches have been described, each method has proven to have its own benefits and drawbacks in terms of the quality and quantity of graphene produced. For example, chemical vapor deposition produces relatively high-quality graphene films but in low quantities, whereas chemical exfoliation of graphite produces large quantities of the poorly conducting monolayer material, graphene oxide (GO). Solution-phase exfoliation of graphite produces graphene platelets with a distribution of thicknesses, but with typical yields of monolayer of less than one percent.

The production of graphene via electrochemical exfoliation in aqueous solution is considered very attractive in terms of scalability, reproducibility, and affordability. However, controlling the quality and properties of the product is often challenging, not least because of the tendency for oxidation of the graphene, especially during anodic exfoliation processes, leading to materials of comparatively low electrical conductivity. The oxidation of water at a graphite surface during electrolysis generates a hydroxyl radical (HO$^-$) and other oxygen radicals. These radicals rapidly react with the graphite surface, resulting in an exfoliated product with oxygen containing functional groups while also introducing a substantial level of defects to the graphene sheets. Indeed, the C:O ratio for graphene obtained by anodic electrochemical exfoliation methods is in the range of 5–10, which is comparable with the C:O ratio found in reduced GO.

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There is, therefore, a need to alleviate the effect of the HO• radical in order to capitalize on the use of anodic electrochemical exfoliation in aqueous solution. To this end, a number of additives or reducing agents to protect graphite against oxidation during electrochemical exfoliation have been attempted. Yang et al. demonstrated the use of a series of reducing agent additives to minimize the effect of HO• during electrochemical exfoliation. In particular, using (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) the authors showed that it was possible to minimize the oxygen content significantly in the final product, achieving a C/O ratio of 25.3. It has been suggested that the HO• preferentially reacts with TEMPO rather than the graphite surface, resulting in exfoliated graphene sheets with low oxygen content (3.8%) and comparatively few defects. The addition of melamine to the exfoliation solution, which was H2SO4(aq), also increased the product C/O ratio from ~16 (without melamine) to 26. The suggested mechanism for the protection of the graphite surface against oxidation was believed to be the adsorption of the aromatic compounds onto the graphene layers. In an alternative approach, Munuera et al. proposed the use of sulfonated aromatic hydrocarbons both as intercalating and reducing agents to combat the oxygen functionalization. They achieved a C/O ratio of between 8.3 and 25. However, the intercalation density of these bulky anions into graphite is expected to be low when compared to simple sulfite ions, thereby affecting the thickness and yield of graphene. Despite these advances, there remains room for improvement for production of high-quality graphene via anodic electrochemical exfoliation.

We describe herein the use of transition metal (Co2+, Ni2+, Fe3+, Mn2+, Ru3+, Ir3+, Ti3+, Pt4+, and Au3+) and other metal ions (Sn4+) as solution additives and show that high-quality graphene, in terms of oxygen content and defect density, can be obtained from this anodic electrochemical approach. Significantly, depending on the identity of the transition metal ions added to the exfoliation solution, the ions acted either as an effective antioxidant for the graphene, or as a metal oxide decorator during electrochemical exfoliation. Surprisingly, the Co(II) salt added to the exfoliation solution acted as an efficient hydroxyl radical scavenger, without functionalizing the exfoliated graphene with cobalt oxides. X-ray photoelectron spectroscopy (XPS) showed that the inclusion of cobalt lowered the oxygen content of graphene by a factor of five when compared to the control (exfoliated in the absence of Co(II) salt) sample. High-resolution transmission electron microscopy and Raman spectroscopy also revealed a substantial reduction of defects and/or holes across the graphene sheets. Ni2+ acted as a spectator ion as it neither reduced the oxygen content nor functionalized the graphene whereas the inclusion of other metal ions (Mn2+, Ru3+, Ir3+, and Sn4+) in the electrolysis solution resulted in decoration of graphene with the oxide of that metal. This simple strategy allows the electrochemical exfoliation of graphite, while also electrodepositing metal oxides such as MnO2, RuO2, IrO2, or SnO2 in a single stage, simultaneous process. For example, the addition of Mn2+ in the electrolyte formed an interconnected honeycomb lamellar structure of MnO2, ca. 2 nm thick, across the graphene sheets. Likewise, the inclusion of Ru3+ formed graphene sheets that were decorated with RuO2 nanoparticles. The combination of the two precursor salts created a uniformly grown Ru–Mn oxide hybrid structure on the graphene sheets. Notably, this bimetallic oxide decorated graphene was found to possess a very high specific capacitance when employed as a supercapacitor (specific capacitance of 500 F g⁻¹) and to function as an efficient electrocatalyst for water splitting showing a separation in overpotentials which is comparable with the values reported for the best bifunctional electrocatalysts. Finally, we demonstrate the use of protic ionic liquids (PILs) as a source of protons for the metal oxide pseudocapacitance.

2. Results and Discussion

2.1. Non-Functionalizing Transition Metal Salts During Electrochemical Exfoliation

The report of Cronin and co-workers has demonstrated that application of a bias voltage exceeding 2.0 V, using symmetrical indium tin oxide (ITO) electrodes in a solution of cobalt (II), generated a selective, metastable electrocatalyst for the oxygen evolution reaction. According to their work, the exfoliation product of Co2+ forms a thin film on the ITO surface which effectively catalyses water oxidation to oxygen gas. They also found that the deposit was only stable on the surface of ITO when the cell was under a voltage bias, whilst at open circuit potential the film was unstable and re-dissolved into the solution. This suggested to us that the inclusion of a Co (II) salt in the exfoliation solution might produce a metastable deposit on the graphite surface which would then insulate it against HO• attack so that the exfoliated graphene product might contain minimal oxygen content without cobalt oxide functionalization. To test this hypothesis, an H-type electrochemical cell was used where the anode (graphite foil) and cathode (graphite rod) compartments were separated by a porous glass frit. Such an electrochemical cell potentially prevents the contamination of the exfoliated graphene samples by cobalt (II) hydroxide since the reduction of water at the counter electrode continuously generates hydroxide ion which reacts with Co2+. It also ensures that any functionalization of the exfoliated graphene is solely due to the co-deposition of metal oxides at the anode rather than due to the physical mixtures from the metal hydroxides generated at the cathode. A combination of 0.05 M CoSO4 (aq) and 0.5 M Na2SO4 (aq) was used as electrolyte where the sulfate anion acted as an intercalating species into graphite to cause exfoliation. During electrolysis, a green precipitate formed in the cathode compartment due to the formation of Co(OH)2 whilst in the anode compartment instantaneous exfoliation of graphite was observed (see inset of Figure 1). This demonstrates that the electrooxidation of Co2+ at the graphite surface did not prevent the exfoliation via sulfate ion intercalation.

To determine whether the anodic product was functionalized with cobalt species or Co2+ merely acted as a HO• scavenger, the exfoliated samples were characterized by XPS and X-ray energy dispersive spectroscopy (EDX). Figure 1A shows the survey scan obtained for the exfoliated graphene product in the presence and absence of the cobalt salt. In each case, the survey scan only showed the signal due to the Cls and O1s, with no...
signals for cobalt species. Sensitivity to Co 2p photoelectrons using 1486.6 eV X-rays photons is ~13 times greater than for C 1s photoelectrons mainly due to the difference in the photoionization cross sections.\(^{[10]}\) Given an upper estimate for sensitivity in XPS is 1% (atomic) for light elements including carbon, an upper limit to the sensitivity for Co 2p is 1/13 (0.08) %. This suggests that that the residual Co level of the exfoliated graphene should be below 0.1 atomic percent. We also note that the oxygen content of the exfoliated product in the presence of CoSO\(_4\) decreased fivefold when compared to the exfoliation in the absence (used as control) of CoSO\(_4\). The addition of CoSO\(_4\) to the exfoliation solution led to a graphene product with a C/O ratio of 36. The increase in oxygen content for the graphene sample relative to the starting graphite foil was only 1.3%, demonstrating that the electrooxidation product of Co\(^{2+}\) plays a crucial role in reducing the extent of graphite surface oxidation. The atomic concentrations of the bulk sample were also analysed by EDX and the data showed that it contained 98% of C and 2% of O, in agreement with the XPS analysis. Ambrosi and Pumera reported much lower C:O ratios (of 8.8, 8.1, and 4.4, respectively) for electrochemically exfoliated graphite samples in Na\(_2\)SO\(_4\) (aq), H\(_2\)SO\(_4\) (aq), and LiClO\(_4\) (aq).\(^{[6d]}\) Parvez et al. reported a C:O ratio of 17 for anodically exfoliated graphene samples in 0.1 M (NH\(_4\))\(_2\)SO\(_4\) and 12 in 0.1 M H\(_2\)SO\(_4\).\(^{[11]}\)

High-resolution C 1s spectra were collected to give more insight to the extent of graphene surface oxidation. The control (no added CoSO\(_4\)) sample shows a shoulder (Figure 1B) at a characteristic binding energy position of carbon functionalization by oxygen-containing groups such as epoxy, hydroxyl, carbonyl, and carboxylic acid.\(^{[11]}\) In contrast, the C 1s spectra of the graphene sample obtained with 50 × 10\(^{-3}\) M CoSO\(_4\) is marked by the absence of any surface functionalization and the spectrum has a shape identical to that of the parent graphite. This shows that the residual oxygen content (1.3%) was most likely from physisorbed oxygen-containing organic material and that the cobalt efficiently protects the graphene surface against oxidation.

Raman spectroscopy has been used to determine the crystallinity of graphitic materials.\(^{[12]}\) A typical Raman spectrum of graphite shows two prominent features located around 1560 cm\(^{-1}\) (G band) and at 2709 cm\(^{-1}\) (D band). The D band can also be seen around 1330 cm\(^{-1}\) if the graphitic materials are defective: the intensity ratio of the D band to the G band may be used as an approximate measure of the sample crystallinity.\(^{[12b]}\) The comparison of the intensity ratio of the D band to the G band (i\(_D\)/i\(_G\)) obtained from large area Raman mapping (10 µm × 10 µm) for the graphene samples obtained in the presence and absence of CoSO\(_4\) (50 × 10\(^{-3}\) M) also supports the conclusion drawn from the XPS analysis (Figure 2A). The i\(_D\)/i\(_G\) of the control sample was 0.98, this value decreased to 0.05 for the graphene sample obtained with added CoSO\(_4\), demonstrating that the latter sample was significantly less defective than the former. High-resolution TEM (HRTEM) images also show the substantial reduction of defects and holes when compared to the graphene exfoliated in the absence of Co salt (Figure 2D–G). HRTEM shows the formation of monolayer graphene and few layer graphene (Figure 2G and Figure S2C, Supporting Information).

The effect of the anion used with the cobalt (II) on the reduction efficiency, as well as the optimum Co (II) salt concentration, was studied and analysed by XPS. Three counter anions were used: sulfate, nitrate, and acetate, all at 50 × 10\(^{-3}\) M concentrations. The result revealed that SO\(_4^{2-}\) produced the graphene with the lowest oxygen content (see Figure 2B). The electro-oxidation of acetate and nitrate may generate reactive oxygen species to functionalize graphene as these anions have lower electrochemical stability than sulfate. Consequently, the sulfate counter ion should be used preferentially as an antioxidant during electrolysis. Following this, the effect of changing the concentration of CoSO\(_4\) was studied. The outcome showed that the oxygen content halved in comparison to the control sample (50 × 10\(^{-3}\) M) when only 3 × 10\(^{-3}\) M CoSO\(_4\) was used (Figure 2C). The oxygen content further deceased.
from 7% to 4% as the concentration of CoSO₄ increased from 3 to 10 × 10⁻³ m. The optimum CoSO₄ concentration was determined to be 25 × 10⁻³ m (2.6% oxygen) as increasing above this concentration did not significantly influence the oxygen content.

The impact of the oxygen content on the conductivity of the graphene film was assessed using a four-point probe resistivity measuring device. The graphene film was made on a PTFE membrane using a syringe pump and, in each case, a 0.1 mg mL⁻¹ graphene dispersion concentration was used to control the thickness of each film. The sheet resistance of the control sample was 845 Ω sq⁻¹ and the resistance decreased to 285, 132, and 67 Ω sq⁻¹ for the graphene exfoliated in

![Figure 2. A) Raman spectra of graphene obtained by electrochemical exfoliation of graphite with and without CoSO₄ and the samples for Raman analysis were prepared by drop-coating the dispersion of graphene on to a Si/SiO₂ wafer. B, C) Survey-scan XP spectra for indicated graphene samples. All peak positions were charge-corrected by setting the binding energy of the C 1s signal to 285 eV and high-resolution TEM images of graphene flakes obtained by electrochemical exfoliation of graphite in (D) 0 × 10⁻³ m CoSO₄ (control), and E–G) 50 × 10⁻³ m CoSO₄. The inset in (F) shows the SAED pattern. In each case, the electrolysis was carried out using 0.5 m Na₂SO₄ (aq) supporting electrolyte.](image-url)
$50 \times 10^{-3}$ m Co(NO$_3$)$_2$, $50 \times 10^{-3}$ m Co(Ac)$_2$, and $50 \times 10^{-3}$ m CoSO$_4$, respectively. The corresponding bulk conductivity value was 2370 S m$^{-1}$ for the control sample and 2.98 $\times$ 10$^4$ S m$^{-1}$ for $50 \times 10^{-3}$ m CoSO$_4$ samples. This demonstrates that the presence of Co$_{3+}$ better protects the sp$^2$ hybridized carbon from functionalization, in agreement with the analysis of XPS data, where sp$^2$ carbon is identified through an asymmetric line shape (as observed in metallic XPS photoelectron peaks) as well as a noticeable shakeup structure at higher binding energy (associated with the $\pi-\pi^*$ transition).[13]

The use of the Ni$_{3+}$, V$_{3+}$, and Ti$_{3+}$ salt neither functionalized the graphene with their respective oxides, nor reduced the oxygen content indicating that those ions acted as a spectator ion (Figure S1, Supporting Information, shown for Ni), whereas the Fe salt reduced the oxygen content of the exfoliated graphene by half (7%) without depositing on the graphite surface as iron oxides (Figure S1C, Supporting Information).

We propose the following mechanism to describe the role of the Co(II) salt during electrochemical exfoliation of graphite. The application of the oxidative potential causes the oxidation of Co(II) salt during electrochemical exfoliation of graphite. In this section, the exfoliation in the presence of oxo-forming metals is investigated. The loading of the desired metal oxides (mono- or bimetallic oxides) can be controlled by varying the concentration of the corresponding salt during electrochemical exfoliation. Figure 3A shows the survey scan XP spectra obtained for graphene samples that were exfoliated in the presence of either $20 \times 10^{-3}$ m Mn(NO$_3$)$_2$, $20 \times 10^{-3}$ m RuCl$_3$, or in the mixture of the two salts ($10 \times 10^{-3}$ m Mn(NO$_3$)$_2$ and $10 \times 10^{-3}$ m RuCl$_3$). The presence of either Mn or Ru (or both) signals along with C 1s and O 1s in the survey scan confirms the functionalization of the graphene with their respective metal species. Close inspection of the O 1s spectrum obtained from the graphene sample exfoliated in the presence of $20 \times 10^{-3}$ m Mn(NO$_3$)$_2$ shows the formation of a new oxygen peak at the characteristic binding energy position of Mn oxide.[17] Moreover, the splitting width of the Mn 3s peak is 4.9 eV which is consistent with MnO$_2$.[17]

EDX analysis of the graphene sample exfoliated in the presence of $20 \times 10^{-3}$ m RuCl$_3$ shows the formation of RuO$_2$. The atomic concentration ratio of Ru (5.2%) to O (12%) from the XPS analysis also supports the formation of RuO$_2$ drawn from the EDX data (Figure S3, Supporting Information). It is interesting to note that the high-resolution C 1s spectra of the graphene functionalized with RuO$_2$ shows the absence of any surface oxidation when compared to graphene functionalized with MnO$_2$ or control samples (Figure 3D). This suggests that the RuO$_2$ acts as a protective layer against graphite oxidation during electrochemical exfoliation. Since RuO$_2$ is the best electrocatalyst for oxygen evolution,[19] it is likely that water oxidation at the RuO$_2$ surface occurs without significant formation of the hydroxyl radical that attacks carbon surfaces. This observation, together with the role of the Co (II) salt, suggests that the use of metal salts where the corresponding metal oxides are good electrocatalysts for water oxidation tends to produce non-oxidized graphene during electrochemical exfoliation by kinetically favoring the oxidation of water. The oxygen evolution reaction via the four electron transfer at graphite surface is much slower than at metal oxides such as RuO$_2$. This was the case if Co$_{2+}$, Ru$_{4+}$, or Ir$_{4+}$ (Figure S4, Supporting Information) salts were employed in the exfoliation solution. The particularly unusual feature of the Co$_{3+}$ case is that it does not functionalize the resulting graphene.

The oxidation state of Mn for graphene samples exfoliated in the presence of $10 \times 10^{-3}$ m Mn(NO$_3$)$_2$ and $10 \times 10^{-3}$ m RuCl$_3$ into the solution according to Equations (1) and (2)[9,16] which explains the absence of Co oxide deposits on the exfoliated graphene surface.

$$2\text{Co}_4\text{O}_4 + 8\text{H}^+ \rightarrow 2\text{Co}_2\text{O}_3 + 4\text{Co}^{3+} + 4\text{H}_2\text{O} \quad (1)$$

$$\text{Co}_4\text{O}_4 + 4\text{H}^+ \rightarrow 2\text{Co}^{3+} + 2\text{H}_2\text{O} + \text{O}_2 \quad (2)$$

2.2. Graphene Functionalized with Transition Metal Salts During Electrochemical Exfoliation

It was shown above that the Co, Ni, and Fe salts acted as non-decorating species during electrochemical exfoliation of graphene. In this section, the exfoliation in the presence of oxide-forming metals is investigated. The loading of the desired metal oxides (mono- or bimetallic oxides) can be controlled by varying the concentration of the corresponding salt during electrochemical exfoliation. Figure 3A shows the survey scan XP spectra obtained for graphene samples that were exfoliated in the presence of either $20 \times 10^{-3}$ m Mn(NO$_3$)$_2$, $20 \times 10^{-3}$ m RuCl$_3$, or in the mixture of the two salts ($10 \times 10^{-3}$ m Mn(NO$_3$)$_2$ and $10 \times 10^{-3}$ m RuCl$_3$). The presence of either Mn or Ru (or both) signals along with C 1s and O 1s in the survey scan confirms the functionalization of the graphene with their respective metal species. Close inspection of the O 1s spectrum obtained from the graphene sample exfoliated in the presence of $20 \times 10^{-3}$ m Mn(NO$_3$)$_2$ shows the formation of a new oxygen peak at the characteristic binding energy position of Mn oxide.[17] Moreover, the splitting width of the Mn 3s peak is 4.9 eV which is consistent with MnO$_2$.[17]
was determined from the splitting width of Mn 3s high-resolution XPS spectrum (Figure S5A, Supporting Information). The splitting width gives 5.5 eV, indicating that the Mn oxide structure is Mn 3O4.[18] Examination of the bulk chemical composition of the hybrid graphene-oxide structure by EDX gives 6%, 9%, 29.6%, and 55.4% of Mn, Ru, O, and C, respectively (Figure S5B, Supporting Information). This shows that the chemical structure of the composite oxide is Mn 3O4–RuO2. The EDX composition also suggests the amount of RuO2 in the composite is 50% greater than that of Mn 3O4, although the composition obtained from XPS analysis indicated that the composite structure contained twice as much Ru as Mn.

Figure 4 shows the SEM, AFM, and STEM-high-angle annular dark field (HAADF) images of the graphene samples that were obtained from 20 × 10−3 M Mn(NO3)2 and 0.5 M Na2SO4. In general, the MnO2 deposit forms a variety of structures including large hemispherical nanowhisker, honeycomb and lamellar nanoparticles, i.e., some discrete and some continuous oxide particles are formed on the graphene sheets. In some cases, the graphene surface was coated with a thin layer of interconnected honeycomb lamellar like structures (Figure 4A-E and Figure S6, Supporting Information). The thickness of the lamellar MnO2 deposits varied between 1 and 2 nm, while the graphene thickness was also between 1 and 2.5 nm (Figure 4B and Figure S7, Supporting Information). The large hemispherical nanowhisker structures consisted of petal-shaped layers of MnO2 (Figure S6, Supporting Information). A magnified STEM image (Figure 4F) shows embedded MnO2 crystals on the graphene surface (Figure S8, Supporting Information, for EDX). The high-magnification STEM image acquired from a part of the lamellar structure is shown in Figure 4G, however, due to complex phase and non-uniform crystal orientation, it was hard to obtain unambiguous phase/structure identification. By contrast to the Mn case, RuO2 formed individual thick particles with many of the nanostructures aggregating on the graphene sheets (Figure 5B,C), suggesting there is a much weaker deposit-substrate interaction in the Ru case. In some places, the RuO2 nanostructures are sparsely distributed over graphene sheets and the average particle size was 2 nm (Figure 5D,F).

The graphene decorated with a combination of RuO2 and Mn3O4 showed different morphology to the graphene decorated with the individual nanostructures. The SEM images show that the RuO2 nanoarchitecture grows inside the MnO2 honeycomb structures with a rod and plate-shaped structure (Figure 6A,B). The average length of the nanorods was 0.5 µm with a diameter of 0.1 µm. Besides these submicrometer-sized features, there are complex nano-sized features at the vicinity of graphene surface (Figure 6C). This complex structure is formed of aggregates of nanoparticles. A magnified STEM-HAADF
image (Figure 6D) shows embedded crystals on the graphene surface. In this image mode, the contrast in the image depends on $Z^2$ ($Z$: atomic number), thus the apparent contrast difference in the image can be related to composition differences. EDX mapping (Figure 6F and Figure S9, Supporting Information) indicated that the oxide structures are uniformly distributed,
but local structure such as Mn/Ru ratio varied, depending on location.

Raman spectroscopy also reflected the formation of functionalized graphene with MnO$_2$ nanostructure. The typical D band, G band, and 2D band of graphene was seen along with three bands at 502, 551, and 655 cm$^{-1}$ due to MnO$_2$(Figure S10, Supporting Information). Powder X-ray diffraction (XRD) data showed weak features besides diffraction peaks from the graphitic structure (Figure S11, Supporting Information). In the case of Mn(NO$_3$)$_2$, a set of prominent peaks was found at 37.3°, 43.0°, and 57.0° which corresponds to the (101), (111), and (211) planes of the $\beta$-MnO$_2$ structure.\[20\] In addition to these peaks, there is broad feature at the lower angle tail of graphite (002) peak. This new peak corresponds to the (002) plane of the $\delta$-MnO$_2$ structure. By contrast to MnO$_2$, only a broad feature at 34.9°, which corresponds to the (101) plane of RuO$_2$, was seen for graphene exfoliated in the presence of RuCl$_3$ (Figure S11, Supporting Information). For graphene obtained from a mixture of Mn(NO$_3$)$_2$ and RuCl$_3$, a similar diffraction pattern to the RuO$_2$ case was found, but the most prominent peaks appeared at 36.7°. The position of the peak is in between RuO$_2$ (101) and $\beta$-MnO$_2$ (101), given that these structures possess the same symmetry (P4$_2$/mnm), this indicates the presence of a mixed oxide phase in the sample.

The role of other transition metal additives including V, Ti, and noble metals (Pt and Au) ions during electrochemical exfoliation of graphite also studied. V$^{3+}$ and Ti$^{3+}$ were found to be spectator ions, while Pt and Au ions decorated the resulting graphene (see Figure S12, Supporting Information, for SEM and XPS). XPS shows that the surface of Pt and Au are oxidized in substantial amount suggesting that the surface functionalities of graphene contains Pt or Au oxides. Overall, the Pourbaix diagram (applied potential versus pH) could help in predicting which metal ion species could be a spectator, an antioxidant or stable oxide forming on the surface of graphene. The voltage we used for exfoliation was excessive enough to oxidize the metal ion additive to its highest possible oxidation state. If the highest oxidation state of that metal is thermodynamically more stable in water than the graphite surface then it will act as a spectator ion. This was the case when V$^{3+}$ was used. Upon electrolysis the green V$^{3+}$ color changed to yellow due the formation of V$^{5+}$, as VO$_2^+$ at the most oxidative potentials and acidic pH, which is soluble in water.

2.3. Electrochemical Applications of Metal Oxide Decorated Graphene

The capacitive behavior of functionalized graphene was assessed using cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge–discharge. These
were compared to the non-functionalized electrochemically exfoliated graphene (EEG) without cobalt (control). Figure 7A shows the CV obtained at 20 mV s\(^{-1}\) of the control, graphene functionalized with 20 \(\times 10^{-3}\) M Mn(NO\(_3\))\(_2\) (G-MnO\(_2\)), 20 \(\times 10^{-3}\) M RuCl\(_3\) (G-RuO\(_2\)), and a mixture of 10 \(\times 10^{-3}\) M Mn(NO\(_3\))\(_2\) and 10 \(\times 10^{-3}\) M RuCl\(_3\) (G-Mn\(_3\)O\(_4\)-RuO\(_2\)) in deoxygenated 1.0 M H\(_2\)SO\(_4\) (aq). The rectangular shape of the CV response and triangular shape of the galvanostatic charge-discharge curve of the graphene-metal oxide composite electrode shows their fast and reversible pseudo-capacitive nature. As shown, the area enclosed by the voltammetric response increased considerably as the electrode changed from EEG to functionalized graphene. As shown in Figure 7A,B, the average capacitance of EEG was 40 F g\(^{-1}\) and this increased to about 100 F g\(^{-1}\) for G-MnO\(_2\) and 210 F g\(^{-1}\) for G-RuO\(_2\) demonstrating the metal oxides’ contribution to the overall capacitance through their pseudo-capacitive behavior, regardless of scan rate. The capacitance increased with increasing loading of RuO\(_2\) on graphene. TGA showed that the use of 7, 20, and 30 \(\times 10^{-3}\) M RuCl\(_3\) during exfoliation produced 16%, 27%, and 38% of RuO\(_2\) loading, respectively (weight loss between \(\approx 300\) °C and 750 °C in the TGA curve was attributed to the decomposition of graphitic carbon). The corresponding capacitance value almost doubled as the loading of RuO\(_2\) increased from 16% to 27% (140 F g\(^{-1}\) in 7 \(\times 10^{-3}\) M RuCl\(_3\) and 230 F g\(^{-1}\) in 20 \(\times 10^{-3}\) M RuCl\(_3\)). At high loading of RuO\(_2\) (38%), its specific capacitance was slightly higher than the 27% loading at lower scan rates, but its capacitance becomes the
same at high scan rates (ν). This demonstrated that 20 × 10⁻³ M RuCl₃ produces the optimum RuO₂ loading for supercapacitor applications during simultaneous electrochemical exfoliation and functionalization of graphene.

The composite sample consisting of graphene, RuO₂, and Mn₃O₄ (G-Mn₃O₄-RuO₂), however, showed an extraordinary capacitance of over 520 F g⁻¹, about twice the value seen for the best performing G-RuO₂ electrodes. This is due to the synergistic effects between the three components where graphene provides conducting channels and an active interface while the electrodeposition process produced high surface area Mn–Ru oxides seen in SEM images. Despite the metal oxide loading of G-Mn₃O₄-RuO₂ (total metal oxide loading was ∼42%) being comparable to that of G-RuO₂ (30 × 10⁻³ M RuCl₃), the series resistance of the former electrode was lower than the latter by more than a factor of ten (0.8 Ω for G-Mn₃O₄-RuO₂ compared to 4.5 Ω for 20 × 10⁻³ M RuCl₃, and 10 Ω for 30 × 10⁻³ M RuCl₃). The decrease in the internal resistance of the bi-metal oxide composite was reflected by the decrease in the ohmic drop (0.05 V in G-Mn₃O₄-RuO₂ versus 0.15 V in G-RuO₂) in the discharge curve obtained at 10 A g⁻¹ (Figure S13, Supporting Information). Furthermore, the charge transfer resistance of G-Mn₃O₄-RuO₂ was 0.3 Ω compared to 17 Ω for the electrode obtained using 30 × 10⁻³ M RuCl₃, which indicates that the redox reactions that contribute to the overall pseudo-capacitance are much faster for G-Mn₃O₄-RuO₂. This is also the case when analysing the relaxation time constant (τ), a constant which reflects the time required to deliver the stored energy and power efficiently.²⁴ The time constant, τ, can also be used to identify the frequency range when the device is dominated by resistive or capacitive behavior.²⁵ For each sample, a τ of 1 s was measured for G-Mn₃O₄-RuO₂ against 6 s for the G-RuO₂ electrode, indicating that the resistive loss for G-Mn₃O₄-RuO₂ is minimal compared to the G-RuO₂. The synergistic interaction between each component was also more evident when comparing their electrocatalytic activity towards hydrogen and oxygen evolution reactions. The polarization curve was recorded at 1600 rpm in 0.1 M KOH for each electrocatalyst. The G-Mn₃O₄-RuO₂ electrode showed enhanced catalytic activity and stability for both reactions when compared to G-RuO₂ or G-MnO₂.(Figure 7E and Figure S14, Supporting Information). The overpotential required to generate 10 mA cm⁻² for OER and HER at G-Mn₃O₄-RuO₂ were 0.3 and 0.24 V, respectively, which stands in contrast to a value of 0.52 V for OER and 0.44 V for HER at G-RuO₂. The RCT of OER at G-MnO₂/RuO₂ was also 10 times lower than the RCT of G-RuO₂ which demonstrates that the kinetics of the OER is much faster at the bimetal oxide-graphene composite. Metal oxides such as Mn₃O₄, Co₃O₄, and RuO₂ are good electrocatalysts for oxygen evolution reaction but poor electrocatalysts for hydrogen evolution.²³ However, metal (Ni, Co, and Fe) phosphide nanostructures have been demonstrated to act as bifunctional electrocatalysts for water splitting, showing overpotentials in the range of 200–400 mV to achieve a current density of 10 mA cm⁻².²⁴ Finally, it is noteworthy that the capacitance retention was over 80% after 5000 cycles (Figure 7D). This suggests no significant metal oxide dissolution or agglomeration occurred, as the electrodeposition process produced a strongly bonded metal oxide to graphene sheets.

The charge storage mechanism of hydrated ruthenium oxide is based on rapid protonation of the oxide.²³ The successive electron transfer at the metal centers (Ru⁴⁺, Ru³⁺, and Ru²⁺) is balanced by proton transfer for the interconversion of the oxide to the corresponding hydroxide.²³⁴ RuO₂ generally has a much higher capacitance than most high surface area carbon-based electrodes when operating in an aqueous acidic media.²³⁶ However, in the absence of a proton source and water (which enhances the conductivity of H⁺) such as in organic electrolytes its capacitance is significantly lower than most carbon-based electrodes.²³⁷ This is due to the inaccessibility of its pseudo-capacitance due to the lack of proton source; the overall capacitance only stems from the electrical double-layer contribution. The specific capacitance of hydrated RuO₂ in acidic media can be as high as 800 F g⁻¹, while the specific capacitance of anhydrous RuO₂ in organic solvent or aqueous media is quoted as being below 30 F g⁻¹.²³⁷,²³⁸ As a result, a supercapacitor device that employs RuO₂ as electrode material in an organic electrolyte suffers from a low energy density.

Here, we used a PIL as source of protons when using RuO₂-based electrodes in organic electrolytes. This ionic liquid is diethylmethylammonium bisulfate ([TEA][BF₄]), which was formed through proton transfer from a Bronsted acid (sulfuric acid) to a Bronsted base (diethylmethylamine).²⁹ Its structure is shown in the insets of Figure 5C. This PIL structure contains protons on both the cation and anion so the pseudocapacitance of RuO₂ can be utilized at the negative and positive electrodes during the charge–discharge process. The PIL was dissolved in acetonitrile to a 1.0 M concentration and used as an electrolyte for RuO₂–Mn₃O₄ symmetrical electrodes, its capacitance was compared to 1.0 M [TEA][BF₄] in acetonitrile (Figure 8). The current measured using an electrolyte containing [TEA][BF₄] at the same ν indicating that the PIL provides H⁺ for the metal oxides redox reaction. This resulted in a specific capacitance which is five times (287 F g⁻¹ at 5 mV s⁻¹) higher than the capacitance of the electrolyte without protons ([TEA][BF₄]). 50 F g⁻¹ at 5 mV s⁻¹). Moreover, the shape of the CV and the charge–discharge curve showed responses that are expected for capacitive behavior for this novel electrolyte. These data demonstrate that PIL-based electrolytes could be used as proton source in metal-oxide electrodes.

3. Conclusions

The catalytic antioxidant function of various transition metal salts has been investigated and applied to the electrochemical exfoliation of graphite. Some of the transition metals (Co²⁺ and Fe⁺³) are used as metal oxide decorators. However, metal (Ni, Co, and Fe) phosphide nanostructures have been demonstrated to act as bifunctional electrocatalysts for water splitting, showing potentials in the range of 200–400 mV to achieve a current density of 10 mA cm⁻².²³⁴ Finally, it is noteworthy that the capacitance retention was over 80% after 5000 cycles (Figure 7D). This suggests no significant metal oxide dissolution or agglomeration occurred, as the electrodeposition process produced a strongly bonded metal oxide to graphene sheets.
ratio. We believe that the use of simple and relatively inexpensive salts paves the way for the scalable production of high-quality graphene. In situ electrochemical exfoliation and decoration of graphene with mono- or bimetal oxide in a single-stage process is also demonstrated where, in particular, the use of Mn$^{2+}$ and Ru$^{3+}$ salts resulted in the deposition of a Mn$_3$O$_4$-RuO$_2$ hybrid structure on graphene that was an efficient electrocatalyst for water splitting and an electrode material for supercapacitors. This simple strategy could be extended to a range of transition metal salts to form graphene-metal oxide composites which can be fine-tuned for various applications. Finally, a PIL was introduced that could potentially be used as a proton source in organic electrolytes for metal-oxide-based supercapacitors.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

A patent application related to the findings of this work has been submitted by the University of Manchester.

**Additional Data**

Original data files can be accessed via http://www.mub.eps.manchester.ac.uk/robert-dryfe-electrochemistry/publications/.

**Keywords**

antioxidant, electrocatalyst, Electrochemical exfoliation, functionalized graphene, protic ionic liquids

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