Sustainable up-cycling of spent electric vehicle anodes into solution processable graphene nanomaterials

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Abstract

A major transition to electric vehicles (EVs) is underway globally, as countries target reductions in greenhouse gas emissions from the transport sector. As this rapid growth continues, significant challenges remain around how to sustainably manage the accompanying large volumes of waste from end-of-life lithium-ion batteries that contain valuable rare earth and critical materials. Here, we show that high-shear exfoliation in aqueous-surfactants can up-cycle spent graphite anodes recovered from an EV into few-layer graphene dispersions. For the same hydrodynamic conditions, we report a process yield that is 37.5% higher when using spent graphite anode as the precursor material over high purity graphite flakes. Increasing surfactant concentration, the average atomic layer number reduces in a similar way to high purity precursors. We find that the electrical conductivity of few-layer graphene produced using the graphite flake precursor is superior, and identify the limitations when using aqueous-surfactant solutions as the exfoliation medium for spent graphite anode material. Using these non-toxic solution processable nanomaterial dispersions, functional paper-based electronics were fabricated, illustrating the potential for end-to-end, environmentally sustainable up-cycling of spent EV anodes into new technologies.

Introduction

Electric vehicles (EVs) have emerged as the primary solution for addressing greenhouse gas emissions in transport, particularly for light-duty vehicles. In the last decade, the number of EVs on the road have grown from almost negligible numbers to ≈ 10M as the urgency for climate action has been recognised by governments and manufacturer’s globally. Over the next ten years, this is projected to increase dramatically from ≈ 10M to ≈ 200M (Figure 1). Both battery electric vehicles (BEV) and plug-in hybrid electric vehicles (PHEV) currently utilise lithium-ion batteries to store and deploy electrical energy. This remarkable rate of EV adoption poses a major waste management challenge as lithium-ion batteries reach their end-of-life.¹

Current material recovery processes are insufficient and there are opportunities to improve the sustainability of the entire battery manufacturing life-cycle.¹ Pyrometallurgy and hydrometallurgy recovery is restricted to high value materials such as Cobalt, Nickel, Copper, and Aluminium with Graphite anodes seen as low recovery value. Despite being placed on the critical materials list and contributing to ≈ 20% of the total lithium-ion battery weight,² graphite is burnt as an energy source, used as a reducing agent in pyrometallurgy, and ultimately disposed of as waste.

Developing effective methods that recycle
Figure 1: The historical and projected growth in battery electric vehicles (BEV) and plug-in hybrid electric vehicles (PHEV) from 2010 to 2030. Data sourced from the International Energy Agency.9

graphite anodes for re-use in new batteries has recently become a focus area for addressing this waste problem.3–5 A complementary option that will be explored in this work is the up-cycling of graphite anodes into graphitic nanomaterials that could have multiple end uses (e.g. electronics, composites, water treatment). Graphite is a layered material containing individual graphene layers held together by van der Waals forces. Various chemical and non-oxidising top-down liquid exfoliation processes have been developed to synthesise few-layer graphene and other graphene-related materials from graphite.6–8 By taking advantage of synthesis methods in the field of two-dimensional materials, it may be possible to develop scalable up-cycling processes to handle the large waste streams from end-of-life EV batteries.

Liquid phase exfoliation techniques have recently been applied to anode graphite recovered from lithium-ion batteries in electronic devices to synthesise graphene, graphene oxide (GO) and reduced graphene oxide (rGO). The techniques vary from ultrasonication-assisted,10 mixed chemical-mechanical approaches,11 and entirely chemical exfoliation methods.12–14 Challenges remain, however, particularly around the environmental sustainabil-

ity of processes that can convert lithium-ion anodes into graphene, GO, and rGO materials.15

Previous approaches have required the use of either toxic solvents (e.g. NMP) in the treatment/pre-treatment step, or are based on other chemical processes (e.g. modified Hummer’s method). In this work, we explore the use of high-shear exfoliation, without harsh chemicals or toxic solvents, to produce solution processable graphene nanomaterials that are then used to fabricate paper-based electronic devices. We assess this green up-cycling approach on anode graphite recovered from an electric vehicle whose battery has reached end-of-life. By doing so, the methods and research outcomes are directly relevant to this rapidly growing industrial sector.

Methods

Electric vehicle graphite recovery

Spent graphite anode material was reclaimed from a Nissan Leaf (generation 1). An illustration of the battery breakdown to the cell level is shown in Figure 2. Graphite was recovered from the copper current collector using a cell teardown process described by Marshall et al.16 The vehicle battery was considered end-of-life (2.5V) and discharged to a 0% state of charge. The resulting anode black mass powder contained the graphite material and a binder (polyvinylidene fluoride, PVDF) with an estimated content < 5%wt. A volume-based median particle size of 21 µm was measured using laser diffraction (Malvern Mastersizer). Previous observations using scanning electron microscopy confirm a large number of particles with diameters ≈ 20 µm within the anode black mass.16

Synthesis of few-layer graphene

Graphite recovered from electric vehicle anodes was dispersed in an aqueous-surfactant solution (V = 160 mL) using de-ionised water (5 MΩm) and sodium cholate (Sigma Aldrich, C1254). The binder was retained in the starting graphite
Few-layer graphene High-shear exfoliation Spent anode material

Material to investigate synthesis without any pre-treatment steps that require toxic solvents such as NMP to wash PVDF from the graphite. The dispersion was subjected to high-shear exfoliation using a cylindrical stirred vessel with diameter 70 mm, height 95 mm and contoured base (Figure 2). A four-bladed impeller of diameter \( D = 55 \) mm was rotated at a speed of \( \omega = 20000 \pm 1500 \) rpm (350W, Kenwood BLP31) resulting in turbulent flow inside the vessel \((Re = \omega D^2/\mu \sim 10^6)\) and shear rates of \(\dot{\gamma} \sim 10^5 \) s\(^{-1}\).\(^17\) This rotational speed was chosen to operate above the critical criterion required to exfoliate few-layer graphene from graphite flakes, \(\dot{\gamma} \approx 10^4 \) s\(^{-1}\).\(^18\)

To avoid overheating the motor and the liquid dispersion, the impeller was rotated for 1 minute followed by 5 minutes turned off. During the off period, the vessel was surrounded by ice and placed in a container inside a freezer at \(-20^\circ\)C. This ensured the dispersion was kept at ambient room temperature for the beginning of each 1 min process interval. A total of 15 process intervals were conducted resulting in an overall process time of \(t_{ex} = 15\) mins for each material synthesis performed.

Finally, the performance of the shear exfoliation up-cycling process for spent EV anode materials was assessed by conducting an equivalent set of experiments on high purity graphite as a benchmark. Graphite flake (Sigma Aldrich, 332461) was chosen as it is one of the most commonly used precursor materials for the production of few-layer graphene in the literature. Laser diffraction measurements were taken and these flakes were found to have a volume-based median particle size of 550 \(\mu\)m. Identical material preparation, high-shear exfoliation, and post-production steps were followed as described for spent EV anode graphite in this Methods section.

**Materials characterisation**

After liquid phase exfoliation, the aqueous-surfactant dispersions were pipetted into centrifugation tubes with a capacity of 15 mL and centrifuged at a relative centrifugal force (RCF) of 243g for 45 mins. The top 5 mL of supernatant contained few-layer graphene and was removed for analysis using UV-visible spectroscopy (PerkinElmer 365). The average atomic layer number \((N)\) was obtained by measuring the extinction spectra \((E(\lambda))\)
of the nanomaterial dispersions and utilising spectroscopic metrics for graphene, \( N = 25(E_{550nm}/E_{max}) - 4.2 \).

Few-layer graphene concentration \((C_{gr})\) was determined by filtering the dispersions through 25 mm diameter PTFE filters with a pore size of 220 nm. The mass of few-layer graphene retained on the filters was measured and then used to calculate the extinction coefficients, \( \varepsilon(\lambda) \). At \( \lambda = 660 \) nm, the extinction coefficient is independent of nanosheet thickness and size. Therefore, this wavelength was chosen when measuring concentration of the few-layer graphene dispersions using the Lambert-Beer relationship, \( C_{gr} = E_{660nm}/\varepsilon_{660nm}L \), where \( L \) is the optical path length of the cuvette (10 mm). The extinction coefficient was measured to be \( \varepsilon_{660nm} = 1014 \) L g\(^{-1}\) m\(^{-1}\) for material produced using the spent EV anode precursor and \( \varepsilon_{660nm} = 1521 \) L g\(^{-1}\) m\(^{-1}\) for the material produced using the graphite flake precursor.

Although there are variations in the values for extinction coefficient across the literature, the value obtained for few-layer graphene exfoliated from the high purity graphite flakes is in close agreement with previous work on liquid exfoliation of the same precursor in aqueous-surfactant solutions.\(^{20}\) The lower value for the extinction coefficient of graphene derived from the spent EV anode precursor may be attributed to the differences in quality of the starting graphite sources. For example, material dependencies were shown recently to have a non-negligible effect on the optical properties of graphene flakes in aqueous solutions.\(^{21}\) Our findings demonstrate that measurements of extinction coefficient are important to consider when testing different graphite sources, even under identical liquid exfoliation conditions and solvents.

## Results and discussion

### High-shear up-cycling performance

The up-cycling performance of high-shear exfoliation in aqueous-surfactants was assessed by comparing the production outputs of the spent graphite anode and high purity graphite flake precursors. The concentration of few-layer graphene products for a range of surfactant concentrations \((C_{sc} \sim 10^{-1} - 10^1 \) g/L\) is shown in Figure 3. In general, across the range of sodium cholate concentrations explored, the product concentration was higher when using the spent EV graphite anode as a precursor. This was most notable for lower surfactant concentrations \((0.05 \leq C_{sc} \leq 1 \) g/L\) where differences of up to \( \sim 10\times \) were found. For surfactant concentrations of \( 1 \leq C_{sc} \leq 20 \) g/L, the concentration of few-layer graphene extracted from the spent anode precursor was comparable to, and up to \( \approx 2\times \) higher than, the graphite flake precursor. The optical extinction spectra for both materials and various surfactant concentrations are shown in Figure 4. Both products were found to have an absorption peak at \( \lambda = 267 \) nm, indicative of the electronic conjugation for graphene.\(^{22}\)

The maximum yields \((C_{gr}/C_i)\) after 15 minutes high-shear exfoliation \((\dot{\gamma} \sim 10^5\) s\(^{-1}\)\) were
1.87%wt (up-cycled EV anode) and 1.36%wt (graphite flake), respectively. Although the absolute yields are low, they are favourable when compared to other scalable non-oxidising liquid exfoliation techniques such as sonication,\textsuperscript{18} microfluidization,\textsuperscript{23} high-shear mixers,\textsuperscript{18} spinning disc and Taylor-Couette type approaches\textsuperscript{24} that produce yields of $0.1 - 3\%$wt for longer processing times of $\sim 1 - 10$ hrs.

We can use the process yield results to estimate the up-cycling material production rate. Using $C_i = 100$ g/L and $V = 0.16$ L, a production rate of $\approx 1.2$ g/hr could be achieved using this high-shear approach. This also compares favourably with other batch shear exfoliation methods. For example, high-shear mixers operating in batch mode can deliver production rates of $\approx 5.3$ g/hr for $C_i = 100$ g/L and $V = 300$ L.\textsuperscript{18} Although the absolute production rate is higher for the latter, the difference in the volume of input resources (water, graphite, surfactant) and process waste is substantially larger by $\sim 10^3$. Alternatively, we can investigate the scale required to achieve the production rates of a batch high-shear mixer. For a similar high-shear stirred vessel to this work, only with larger process volumes up to $\approx 1$ L, Pérez-Álvarez et al. showed that few-layer graphene concentration follows the scaling relationship, $C_{gr} \sim \gamma \sim \omega^{3/2}V^{-1/2}$, above the critical exfoliation criteria.\textsuperscript{17} Applying this scaling, we estimate an up-cycling production rate of $\approx 5$ g/hr with a process volume of $V = 3$ L. This is only 1% of the volume required by high-shear mixing in batch operation, indicating that high-shear up-cycling of spent graphite anodes is a promising and environmentally sustainable approach.

In terms of end-use considerations, equally significant is that the maximum yield using spent graphite anode was obtained for a surfactant concentration that was one order of magnitude lower than for graphite flakes. Indeed, we also measured the concentration for high-shear up-cycling in water only ($C_{sc} = 0$), and this resulted in a yield of 0.69%wt. Considering residual surfactant can adversely impact material properties and can be challenging to remove from solution processed functional devices (e.g. requiring high temperature annealing\textsuperscript{25}), high-shear up-cycling has potential to provide sustainable synthesis of few-layer graphene with low additive requirements.

Interestingly, two different characteristics were observed for each precursor. The up-cycled product featured a bimodal concentration profile, whereas the few-layer graphene produced from graphite flakes contained a single peak in concentration at $C_{sc} \approx 4$ g/L. The occurrence of a single peak in concentration can also be seen in previous studies on liquid exfoliation of graphite in aqueous-surfactant solutions using sonication\textsuperscript{20} and high-shear exfoliation.\textsuperscript{17,26} Recently, using WS$_2$ as a model system, Griffin et al. showed that a fall-off in nanosheet concentration occurs at $\sim 10$mM for all ionic surfactants.\textsuperscript{27} The authors measured reductions in ionic conductivity of the aqueous-surfactant dispersions in this region and hypothesised this behaviour to be due to electrostatic screening. The sharp decrease in few-layer graphene concentration shown in our work for $C_{sc} > 5$ g/L coincides with $C_{sc} \approx 10$mM. The few-layer graphene produced by up-cycling also follows a similar reduction in concentration in this region ($C_{sc} \sim 10$mM). This suggests the same nanosheet destabilising mechanism at $C_{sc} \sim 10$mM also applies to the solution processing of spent graphite anode materials in aqueous-surfactants.

In the low surfactant concentration region ($0.05 \leq C_{sc} \leq 1$ g/L), the primary (largest) peak in $C_{gr}$ for the up-cycling process occurs ($C_{sc} = 0.1$ g/L). This contrasts the trend observed for shear exfoliated high purity graphite flakes, where the dispersions have poor stability and the lowest few-layer graphene concentrations. Further investigation into this finding is necessary, however, the enhanced concentrations using spent anode precursors may be attributed to: 1) the presence of significantly more edge sites on the sphericalised particles for intercalation and delamination to occur; 2) graphite expansion from the intercalation of lithium between layers during charge/discharge battery cycles; and 3) increased wetability of the PVD binder due to the presence of the surfactant.
Expanding on 1)-3) above, the sphericalised graphite particles from the EV anode are much smaller than the flake graphite particles, with a D50 of 21µm compared to 550µm. As part of the sphericalisation process, these particles are jet milled to create a morphology which also contains more sites for intercalation and delamination of layers than the graphite flakes. Also, during the operational lifetime of the battery, lithium ions intercalate the graphitic layers in the anode, weakening the van der Waals attractive force. It has been suggested that this process can expand the layer spacing by an average of 3.5% (0.352 nm) and up to 14.7% (0.39 nm).11 Chemical and thermal expansion of graphite as a pre-treatment step in the synthesis of graphene and graphene-derived materials (e.g. GO, rGO) is a method known to improve production output,7 therefore the presence of dilated layers in the anode graphite would also benefit the exfoliation process. Finally, the PVDF binder is hydrophobic which should reduce the dispersability of graphitic particles in water. However, anionic surfactants have been shown to have an affinity to PVDF and increase wetability below the critical micelle concentration (CMC).28 An increased wetability may also play a role in the enhanced anode material dispersibility that is observed here below the CMC for sodium cholate. Nevertheless, the high recovery performance is encouraging and further research in this low surfactant region would help optimise the mechanisms which enhance concentration using spent graphite anode material.

Variations in surfactant concentration modified the extinction spectra for both graphene materials in the UV wavelength region (Figure 4). For few-layer graphene, this change in shape is a signature of a change in the average number of atomic layers.19 The number of atomic layers is plotted against surfactant concentration in Figure 5 and a similar trend was observed for both few-layer graphene materials. Thicker sheets are present in low surfactant concentration dispersions. The thickness remains relatively constant up to \( C_{sc} \sim 1 \text{ g/L} \) and then decreases further as surfactant concentration increases. This corresponds with the threshold of \( C_{sc} \sim 10\text{mM} \) and aligns with the previous observations for \( C_{gr} \) noted above, and for other 2D materials synthesised from high purity precur-
This demonstrates that the atomic layer number of few-layer graphene exfoliated from spent graphite anodes recovered from EVs can also be tuned using surfactants. The rate of change in layer number with $C_{sc}$ was found to be lower for the up-cycled material. At the highest $C_{sc} = 20 \text{ g/L}$, the differences in layer number increased from $\Delta N \approx 2$ to $\Delta N \approx 3$. Overall, it appears that few-layer graphene dispersions produced from graphite flakes have a lower average number of layers than the up-cycled product. This suggests that for the same hydrodynamic conditions and aqueous-surfactant solutions, the quantity of few-layer nanosheets produced from spent EV anodes is less than for the high purity graphite flakes. Shear exfoliation using turbulent flows erodes the outer surfaces of graphite flakes to produce few-layer graphene. The resulting few-layer sheets continue to reduce in thickness by rate-controlling processes that span the entire range of turbulent energy-containing flow structures down to the Kolmogorov length. The binder layer that coats the surfaces of graphite anode particles, and smaller exfoliated platelets, potentially acts as a barrier for slip and peel mechanisms of delamination to proceed at the nanoscale.

The spectroscopic metric used to calculate $N$ is based on an empirical correlation that predicts average layer number to within 15% for a number of different graphite precursors. The shaded regions in Figure 5 represent the combined correlation and experimental uncertainties. The bounds of these uncertainties in average layer number for the different precursor materials overlap, and an analysis focusing on individual nanosheet size distributions would ultimately confirm the thickness statistics (e.g. using AFM). However, these differences in material quality (thickness) are in agreement with measurements of electronic properties presented in the following section.

**Application to paper electronics**

Maintaining the theme of environmentally-compatible processes, we explored the application of up-cycled graphene materials for fabricating paper printed circuit boards. The electronic properties were investigated by solution-processing graphene dispersions to create paper-based conductive thin films. Graphene inks were prepared using shear exfoliation in de-ionised water/sodium cholate followed by centrifugation and spray deposition onto paper substrates (100% cellulose, acid-free, 300 gsm, cold-pressed). An illustration of the spray deposition process is shown in Figure 6A.

With few-layer graphene yields of the order $\sim 1\% \text{wt}$ after a 15 minute exfoliation process time, the mass of the remaining graphite is large. However, the number of graphite particles retained in non-centrifuged liquid phase exfoliated dispersions has been found to be low ($\approx 5.5\%$) compared to few-layer graphene nanosheets with $N \leq 10$. This suggests the graphite mass is dominated by a small number of poorly exfoliated particles. To remove these, the as-prepared dispersions were centrifuged at a RCF = 115g for 20 minutes, following a similar approach recently described for biocompatible few-layer graphene inks. As these formulations contain thicker nanoplatelets, we refer to

![Figure 5: Variation in the average number of atomic layers with surfactant concentration for few-layer graphene dispersions produced using spent EV graphite anode and flake graphite precursors.](image-url)
the inks as graphene-related material (Grm) to distinguish them from the few-layer graphene dispersions formulated at RCF = 243g.

Inking concentration was increased above 1 g/L by exfoliating spent graphite anode material at $C_i = 50$ g/L and using a surfactant concentration, $C_i/C_{sc} = 100$, corresponding to the peak $C_{gr}$ shown in Figure 3. This resulted in an ink concentration, $C_{Grm} = 1.66$ g/L. To obtain an equivalent ink concentration from the high purity graphite flake precursor, exfoliation was first performed using $C_i = 100$ g/L and $C_i/C_{sc} = 20$, resulting in $C_{Grm} = 2.8$ g/L. This “Flake Grm” product was then diluted to match the concentration of the up-cycled “EV Grm” product before spraying the paper substrate.

A 90 mm × 40 mm area was airbrushed with a supply pressure of 20 psi, resulting in a graphene material deposit of 0.184 g/m$^2$ per spray pass. Multiple spray passes were used to create flexible paper substrates that were electrically conducting on the coated side and insulating on the other. The coatings were physically robust with strong adherence to the paper backing and the ability to withstand bending and folding. To accelerate the drying process, air at a temperature of 200°C was blown over the paper using a heat gun, evaporating the water solvent after each spray pass. An example of a paper substrate with 100 passes of shear exfoliated graphite anode material is shown in Figure 6B. Assuming negligible porosity and uniform thickness, the minimum thickness limit of the dried nanoplatelet film can be estimated to be $\approx 8\mu$m for 100 spray passes. However, some porosity is likely to exist, and the actual film thickness will be larger and contain variability from the coating method. Although the cold-pressed paper substrate has visible roughness that can contribute to this variability, it also provides increased substrate porosity (over hot-pressed) that is advantageous for wetting and nanoplatelet film reproducibility.31 This is confirmed by the low magnitude error bars in Figure 6C which include the standard deviation in electrical resistance for different nanoplatelet films tested. The variation in the electrical resistance was found to be below 12% for all Grm coatings.

The sheet resistances of various spray coated paper substrates were measured in accordance to the transmission line method.25 Copper tape electrodes (75µm thickness, 6 mm width) were positioned in parallel and bonded to the Grm coated paper ($W = 40$mm) using low contact resistance adhesion ($R = 0.001\Omega$). The electrical resistance was measured between electrodes spaced at various distances, $L$, apart (Keithley model 2000). The sheet resistance was then determined from the slope of the linear trend between $L/W$ and paper resistance, shown in Figure 6C. The sheet resistances span $\sim 1 - 10$kΩ/sq which is similar to that observed in other studies investigating spray coated graphene inks on paper substrates.31

Using the Flake Grm as the reference, the sheet resistance was found to be $\sim 10\times$ higher for the EV Grm coating. This is due to a combination of factors including thicker and smaller nanosheets, the presence of residual anode binder in the nanosheet network, and the potential presence of nanosheet defects. Under the same shear exfoliation conditions, Figure 5 shows that the number of layers in the up-cycled graphene dispersions are greater than when using high purity graphite flakes (by $\Delta N \approx 2 - 3$). To explore this further, we isolated the fraction of few-layer graphene contained in the shear exfoliated Grm inks by performing an additional centrifugation step at RCF = 243g and 45 mins. We measured the extinction spectra for both RCF = 115g and RCF = 243g and compared the spectroscopic ratio $\varepsilon_{550nm}/\varepsilon_{267nm}$ as a proxy to illustrate the changes in atomic layer number (Figure 6D). The fraction of few-layer graphene ($N \approx 10$) in the EV Grm ink was found to be $\approx 64\%$wt. In contrast, the graphitic material within the Flake Grm ink is dominated by few-layer graphene nanosheets ($N < 10$) including a significant fraction with $N = 8$ ($\approx 64\%$wt). This difference in composition impacts the electronic properties of the deposited film and results in a higher sheet resistance for the up-cycled spent EV anode material.

The conductance of the thin film produced
Figure 6: Performance of up-cycled EV anode material. (A) Schematic of thin film deposition of graphene-related nanoplatelet materials (Grm) onto a paper substrate using airbrushing. (B) An image of a Grm coating produced from shear exfoliated spent graphite anode material and 100 spray passes. (C) Electrical resistance of various Grm coatings spray deposited onto paper. (D) Comparison between the spectroscopic ratio \( \varepsilon_{550\text{nm}} / \varepsilon_{267\text{nm}} \) for EV Grm and Flake Grm dispersions, with the ratios corresponding to an average layer number of 8 and 10 highlighted. The same Grm concentration was used for all inks during airbrushing \( (C_{\text{Grm}} = 1.66 \text{ g/L}) \). These were prepared using \( C_{i} / C_{sc} = 100 \) (EV), \( C_{i} / C_{sc} = 20 \) (Flake), \( \omega \approx 20000 \text{ rpm} \) for \( t_{ex} = 25 \text{ mins} \), and RCF = 115g for 20 minutes.

From EV Grm increases almost fourfold when the number of spray passes is doubled to 200. This highlights that further reductions in sheet resistance towards \( \sim 1\text{k}\Omega/\text{sq} \) are possible by continuing to increase the number of spray passes. Of course this would be at the expense of using more material, however, the maximum yield was 37.5% higher for spent graphite anode. A sustainable pre-treatment step to remove the PVDF binder and additives prior to shear exfoliation would also reduce sheet resistance for the Grm ink. Furthermore, size selection and surfactant removal have recently been shown to have significant influences on the electrical conductivity (\( \sim 10 \times \) changes) of graphitic nanoparticulate materials exfoliated in water/Triton X-100 surfactant solutions. Similar approaches may also work with liquid exfoliated spent graphitic anode materials, maximising the conductivity of up-cycled functional inks where graphitic nanoparticles, additives and surfactants are present.

Although the electrical conductivity of the paper coatings was superior using high purity graphite flakes, contemporary electronic circuits rely on a suite of different compo-
Figure 7: A basic paper circuit board fabricated using shear exfoliated anode material recovered from an end-of-life electric vehicle battery. (A) Paper layers and light-emitting diode (LED) circuit. (B) Functioning electronics powered using a 12 VDC supply. (C) Top down view of the paper circuit board assembly indicating an overall thickness of 1.5 mm.

Transport and materials (conductors, insulators, semi-conductors). We exploited the differences in electronic properties between EV Grm and Flake Grm solution-processed thin films to fabricate a simple paper circuit board with a white light-emitting diode (Figure 7). Paper substrates were coated using the same approaches described above and illustrated in Figure 6A. The ground plane was coated with Flake Grm and the power plane was coated using up-cycled EV Grm ink. The paper substrates were then cut to size and glued together to create insulator-conductor multilayers with an overall circuit board thickness of 1.5 mm. The EV Grm layer provided a dual purpose, acting as the power plane for the +ve LED pin to connect to, and as a ballast resistor that prevented over-current when using a 12 VDC supply. This simple example demonstrates that shear exfoliation in aqueous-surfactant solutions can be used as a green approach to up-cycle battery anode waste and contribute to material circularity for electric vehicles.

Conclusion

This work demonstrates that high-shear exfoliation in aqueous-surfactants is a viable approach for up-cycling spent graphite anodes from electric vehicles into solution processable graphene. Nanomaterial yield was found to be comparable to, and in most cases higher than, that obtained using high purity graphite flakes as a precursor. The maximum concentration recovered using this up-cycling approach was 37.5% higher than the peak concentration of few-layer graphene obtained from graphite flakes. Spectroscopic measurements suggest that the average atomic layer number in aqueous-surfactant dispersions is 2-3 atomic layers less when using the high purity graphite flake precursor. The spheri-calised graphite morphology together with the
presence of the PVDF binder impact production output, particularly at low surfactant concentrations of $C_{sc} < 10\text{mM}$. At concentrations above this, the surfactant influences the up-cycled product concentration and layer number similarly to few-layer graphene exfoliated from graphite flakes. Finally, we investigated the use of up-cycled graphene-related material for fabricating paper electronics. The sheet resistance of thin films formed from up-cycled material is an order of magnitude higher, which may be addressable using alternative solvents to remove the binder and any additives. However, the environmental sustainability of the proposed water-based liquid processing techniques is advantageous over chemical treatments or traditional toxic solvent use. Furthermore, lithium ion batteries also utilise different binders that are dissolvable in water (e.g. carboxy methyl cellulose) and graphite sources (e.g. natural, synthetic) which provide opportunities for improvements without sacrificing the sustainability of the high-shear up-cycling process.

Acknowledgement This invited contribution is part of the I&EC Research special issue for the 2022 Class of Influential Researchers. This work was supported by a RAEng/Leverhulme Trust Research Fellowship and The Royal Society Research Grant (Ref: RGS\R2\202379). We also acknowledge support from the Faraday Institution under the ReLIB project FIRG005 and FIRG006.

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