High quality, low-oxidized graphene via anodic exfoliation with table salt as an efficient oxidation-preventing co-electrolyte for water/oil remediation and capacitive energy storage applications

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Abstract

The production of graphene through anodic exfoliation of graphite in water is regarded as a competitive approach in the efforts to scale-up the manufacturing of this two-dimensional material for different practical uses. However, issues related to oxidative attack of the nanosheets inherent to this delamination process have traditionally precluded the attainment of high quality materials, with the use of proper electrolyte additives as oxidation-preventing agents being proposed as a possible way out. Here we demonstrate that sodium chloride (table salt) can be used as a highly efficient additive (co-electrolyte) of common sulfate-based electrolytes, yielding anodically exfoliated graphene with minimal oxidation (O/C ratio ~ 0.02 - 0.03) and thus a high structural quality. As an oxidation-preventing co-electrolyte, sodium chloride clearly outperformed other tested additives, including sodium borohydride, sulfite, citrate, bromide and iodide, ascorbic acid or ethanol, as well as other recently reported chemical species of a more complex nature and/or less readily available. The apparently contradicting ability of the chloride anion to avert oxidation of anodic graphene without negatively interfering with the exfoliation process itself was also discussed and ultimately ascribed to the different chemical reactivity of graphite edges and basal planes. The as-prepared, low-oxidized graphene exhibited a notable adsorption capacity towards organic dyes in aqueous solution (e.g., $\sim 450 \text{ mg g}^{-1}$ for methyl orange), a substantial ability to absorb oils and non-polar organic solvents (15 - 30 g g^{-1}), and displayed a good capacitive energy storage behavior (e.g., $\sim 120 \text{ F g}^{-1}$ at 0.1 A g^{-1}), all without the need of any post-processing steps that are so common for graphene-based materials. Overall, the demonstration that low-oxidized anodic graphene can be obtained by resorting only to inexpensive and widely available reagents should facilitate the implementation of this methodology in the industrial manufacturing of high quality graphene for several applications.

Keywords

Graphene

Electrochemical exfoliation

Energy storage

Water remediation

1. Introduction

The electrochemical exfoliation of graphite has emerged in recent years as a very promising approach in the efforts to tackle one of the most pressing issues that hinder the widespread implementation of graphene in real-life applications, namely, its large-scale production [1-5]. Such an approach boasts a number of assets that are not always present in other potentially scalable methods of graphene production, such as simplicity of operation, versatility (e.g., in terms of electrolyte choice), alacrity (short processing times) and cost-effectiveness. The electrochemical process of graphite delamination to give graphene nanosheets can be carried out under either cathodic or anodic conditions [3,4], or by a combination of both [6,7]. Cathodic exfoliation typically makes use of lithium or alkylammonium salts in organic solvents as the electrolytic system, yielding graphene materials of a high structural quality and limited oxidation (O/C atomic ratios of ~0.03-0.08) [8-10]. However, it tends to suffer from low exfoliation degrees (flakes frequently comprising more than 5 monolayers) and yields. Anodic exfoliation, on the other hand, is generally accomplished in water with inorganic acids or their salts as the electrolyte, which is attractive from an environmental and practical point of view [3,4]. Further, the anodic approach is normally more efficient than its cathodic counterpart in terms of both delamination degree (single- to few-layered nanosheets) and yield.

Unfortunately, anodic graphene has a strong tendency to oxidize during exfoliation, due to attack by oxygen radicals generated from the oxidation of water molecules at the graphite anode. For common electrolytes (e.g., sulfuric acid, sulfate salts and others), graphenes with O/C ratios in the 0.10-0.20 range are usually obtained [11-16]. This extent of oxidation compromises the structural quality of the material, and thus constitutes a serious drawback of the anodic approach that limits its wider practical utility. Still, recent studies have provided evidence that such an oxidation is not an unescapable outcome of anodic exfoliation, and that indeed it can be largely avoided by resorting to appropriate electrolytes and/or electrolyte additives [17]. To this day, only a few chemical species have been identified to be useful towards this purpose, specifically (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) [18] and melamine [19] as additives of sulfate-based electrolytes, as well as sulfonated naphthalene as an electrolyte itself [20]. A significant problem of these organic species is that they are relatively complex and expensive compounds, thus hindering their prospects of use in the industrial

production of graphene. Moreover, they can strongly adsorb on the resulting graphene product, making purification of the latter difficult [20]. Hence, the identification of much simpler, readily available, low-cost and easy-to-remove species with a similar or even better oxidation-preventing ability to give high quality, oxide-free anodic graphene nanosheets would be highly desirable, but has so far not been attained.

We report here the finding that a readily available and extremely simple substance, namely NaCl (table salt), is a highly efficient oxidation-preventing additive (co-electrolyte) towards the anodic exfoliation of graphite. The use of NaCl as an additive of sulfate-based electrolytes is shown to afford anodic graphene with the lowest degree of oxidation documented to date (O/C ratio of ~0.02-0.03) and a high structural quality. Indeed, these features are very similar to those typical of pristine graphene flakes obtained by direct, liquid-phase exfoliation of graphite via ultrasound or shear forces, but with the additional advantage of a process that exhibits higher exfoliation yields and degrees. Concerning its potential utility application-wise, the as-obtained graphene product is shown to be an efficient adsorbent of industrial dyes from the aqueous phase as well as of non-polar organic solvents/oils, and also exhibits a good performance as an electrode for capacitive energy storage. Owing to the obvious practical advantage of NaCl over other electrolyte additives, we believe this work will strengthen the position of electrochemical exfoliation as a method of choice in current efforts to industrialize the production of high quality graphene.

2. Results and discussion

2.1. NaCl as an efficient electrolyte additive (co-electrolyte) towards low-oxidized anodic graphene

The aqueous anodic exfoliation of graphite to give graphene nanosheets is generally considered to rely, at least in its early stages, on oxidation processes that assist in the interlayer expansion at edges, grain boundaries and other structural defects of the graphitic lattice, thus facilitating the subsequent intercalation of anions from the electrolyte together with water molecules (hydrated anions) to induce an efficient delamination [4,21]. The oxidative attack of the graphite electrode is triggered by highly reactive oxygen species, such as hydroxyl radicals ($\cdot\text{OH}$), generated from the anodic oxidation of water molecules. Hence, the inclusion of chemical species in the electrolytic medium as additives or co-electrolytes with an ability to neutralize (i.e., reduce) these oxygen radicals could be an effective strategy to curtail the oxidation of

the anodically derived graphene nanosheets [17]. Obvious candidates for this role are certain organic and inorganic compounds that are widely employed as reducing agents or antioxidants in chemical reactions, such as NaBH_4 or ascorbic acid. However, their efficacy in preventing oxidative attack during anodic exfoliation could be compromised by kinetic and other factors that are difficult to ascertain, and they could also negatively interfere with the delamination process itself [18]. Alternatively, we hypothesize that chemical species without a well-known ability to act as reductants or antioxidants, but having a reduction potential lower than that of the oxygen radicals generated during the anodic process, could be efficient in averting oxidation of the exfoliated nanosheets. In particular, we focus our attention on NaCl as a potential oxidation-preventing electrolyte additive. NaCl is a very common and low-priced commodity, making its use especially attractive with a view to the scaled-up production of graphene, and the standard reduction potential of the relevant redox pair (i.e., the Cl^-/Cl_2 pair, +1.37 V) is lower than that of the $\cdot\text{OH}/\text{OH}^-$ pair (+1.9 V) [22,23]. Indeed, oxidation of the Cl^- anion by $\cdot\text{OH}$ radicals in aqueous medium to give OH^- anions or water molecules has been well documented in past studies [24].

As schematically depicted in Fig. 1a, we carried out a series of benchmark exfoliation experiments by which a graphite foil piece (working electrode) was set to a positive voltage (10 V) relative to a platinum foil (counter electrode). The process was conducted in an aqueous solution containing 0.1 M Na_2SO_4 as the main (exfoliating) electrolyte and a given molar concentration of another chemical species (e.g., NaCl) as the prospective oxidation-preventing agent [see Electronic Supplementary Material (ESM) for details on the experimental procedure]. Na_2SO_4 was chosen as the main electrolyte owing to the well-known ability of the sulfate anion to intercalate and expand the interlayer space of graphite under anodic conditions [25-28]. For comparison purposes, additives or co-electrolytes other than NaCl were tested in the exfoliation experiments, including KCl , KBr , KI , NaBH_4 , Na_2SO_3 , sodium citrate, ascorbic acid and ethanol. KBr and KI were selected because the redox potential of the Br^-/Br_2 and I^-/I_2 pairs (+1.09 and +0.54 V, respectively [23]) is also lower than that of the $\cdot\text{OH}/\text{OH}^-$ pair, while NaBH_4 , Na_2SO_3 , sodium citrate, ascorbic acid and ethanol are common reductants/antioxidants. Upon application of the bias voltage the graphite foil anode was seen to swell and enlarge in thickness, giving rise to exfoliated products in significant quantities (Fig. 1b) made up of worm-like, highly expanded particles (Fig. 1c) with a morphology of very thin, corrugated layers separated by micrometric or even

nanometric voids (Fig. 1d). This morphology is characteristic of anodically delaminated graphites [21,29]. The as-exfoliated material was then transferred to the liquid phase with the aid of a mild sonication step, finally yielding colloidal suspensions of graphene nanosheets in, e.g., water/isopropanol mixture, *N,N*-dimethylformamide or water with flavin mononucleotide dispersant that were stable for weeks (Fig. 1e; see ESM for details). The UV-vis absorption spectra of the suspensions in water/isopropanol (Fig. 1f) exhibited a peak centered at ~270 nm together with strong absorbance in the whole measured wavelength range above 270 nm. This result was consistent with the presence of extended, electronically conjugated sp^2 -based domains in the dispersed material, as reported previously for graphenes with limited oxidation (e.g., highly reduced graphene oxide and pristine graphene flakes) [30,31].

To quantify the impact of the abovementioned additives on the extent of oxidation of the exfoliated nanosheets, their corresponding dispersions in water/isopropanol were deposited onto metallic sample holders, forming thin graphene films that were subsequently investigated by X-ray photoelectron spectroscopy (XPS). Table 1 shows the O/C atomic ratio measured by this technique for anodic graphenes obtained at different molar concentrations of the additives. In the absence of any additive (control sample; only 0.1 M Na_2SO_4 was used as electrolytic medium), this ratio was determined to be ~0.09. It was generally observed that at low molar concentrations (e.g., 0.01-0.02 M), the additives had a detrimental effect on the oxidation of the nanosheets, i.e., the resulting graphenes tended to exhibit O/C ratios higher than that of the control sample (~0.11-0.18 vs 0.09). On the other hand, concentrations around 0.1 M of the NaCl and KCl additives afforded graphenes with a remarkably reduced degree of oxidation, boasting O/C ratios as low as 0.02-0.03. Indeed, the latter figures were among the lowest ever documented for anodically exfoliated graphenes [17-20]. For example, using TEMPO and melamine as additives, O/C ratios around 0.04 were attained [18,19]. but different to the case of these previous reports, the present results were obtained using readily available, very low-priced and environmentally friendly substances in the electrolytic process. The amount of oxygen in these samples was very close to that present in the starting graphite foil material (O/C ratio ~0.01), implying that anodic oxidation of the graphite electrode could be kept to a minimum using the chloride-based additives. Noticeably, for ionic additives incorporating anions other than Cl^- , specifically Br^- , I^- and SO_3^{2-} , as well as for ethanol, the use of concentrations in the order of 0.1 M (or even higher) did not bring about large reductions, if any at all, in the

extent of oxidation of the corresponding graphene samples compared to the control one. For some compounds (NaBH_4 and ascorbic acid), swelling and expansion of the graphite anode did not even take place to any substantial extent at concentrations of 0.1 M, and thus no exfoliated products were procured. In the case of 0.1 M sodium citrate, only a small amount of exfoliated material could be obtained. We have also determined the yield of graphene material produced both in the absence (control sample) and presence of Cl^- (i.e., 0.1 M Na_2SO_4 plus 0.1 M NaCl or KCl). For graphite foil pieces with a thickness around 500 μm , the measured yields were ~ 13 and 10 wt% for anodic exfoliation in the absence and presence of Cl^- , respectively. First of all, we note that in general these yield values cannot be directly compared with those reported in the literature by other groups, because exfoliation yields are dependent, among other factors, on the thickness of the graphite piece used in the electrolytic process [28]. Indeed, we have used a graphite foil that is several times thicker than those used in other reports [21], implying that the yield should be several times lower. Second, the yield values measured here in the absence and presence of Cl^- were of a similar magnitude (somewhat lower for the latter), indicating that the presence of this additive in the electrolyte (at the relevant moderate concentration of 0.1 M) does not hamper the exfoliation process to a very significant extent.

It is currently unknown why the chloride-based additives perform so efficiently in averting the oxidation of anodic graphene in a certain range of concentrations around 0.1 M, whereas at lower molar concentrations all the tested additives appear to promote graphene oxidation. We can expect a number of different competing processes that arise from complex interactions between the graphite electrode, main electrolyte, additive and water molecules to be in place during the anodic treatment. In turn, such processes and interactions are probably dependent, among other factors, on the electrolyte and additive concentration. This hypothesis was supported by the observation that at sufficiently high additive concentrations (e.g., NaBH_4 and ascorbic acid at 0.1 M, but also NaCl and KCl at 1 M, and ethanol at 3 M), exfoliation of the graphite anode did not even take place, suggesting that these compounds could inhibit intercalation of the sulfate anion or, alternatively, certain subsequent reactions that trigger expansion of the interlayer space in the anode. The complexity of the involved mechanisms is also made apparent by noting that the oxidation-preventing ability of the halide-based additives did not correlate directly with the redox potential of the corresponding halide/halogen pair. If such a correlation were indeed in place, we would expect the KBr and KI additives to

yield graphenes with a lower oxidation degree than that afforded by the NaCl/KCl additives by virtue of the lower redox potential of the Br^-/Br_2 and I^-/I_2 pairs relative to the Cl^-/Cl_2 pair, but that was not the case. It is thus very likely that kinetic factors play a relevant role in the reactions occurring between different chemical species during intercalation and exfoliation of the graphite anode.

The present results also raise the apparently contradicting question of why the exfoliation yield was not critically affected by the addition of 0.1 M NaCl (or KCl) while at the same time this additive prevented to a large extent the oxidation of the graphite anode, which on the other hand is assumed as a prerequisite for exfoliation to occur. In this regard, a couple of points have to be considered. First, it is quite likely that the only strict requirement for anodic exfoliation to proceed is the oxidation of the graphite edges, but not of its basal planes. This oxidation would locally increase the interlayer spacing at the graphite edge, thus facilitating the penetration of hydrated anions from the electrolyte. Once a number of hydrated anions have been inserted into the interlayer space at the edges, further oxidation of the graphite lattice (i.e., at locations other than the edges) would not be strictly necessary, as the inserted ions and water molecules themselves (or their electrolyzed products) would readily trigger the interlayer expansion (exfoliation) of the material increasingly further away from the edges by acting as a sort of wedge. Under this scenario, only the edges of the exfoliated graphene nanosheets would have to be necessarily oxidized for anodic exfoliation to take place. Considering that the fraction of edge atoms in graphene nanosheets with sizes in the micrometric and submicrometric range is low (a few percent at most), the overall extent of oxidation in the resulting nanosheets should be correspondingly small, provided that only edges become oxidized. Second, as suggested above, we believe that the oxidation-preventing action of the Cl^- anions must be driven not only by thermodynamic but also by kinetic factors regarding the reactions that take place between Cl^- anions, oxygen radicals and graphite anode. More specifically, it is well known in carbon science that graphite edges and basal planes possess quite different reactivities towards attack by oxygen radicals [32], the former being substantially more reactive than the latter. Such a difference in reactivity should imply a faster attack of the edges by the oxygen radicals compared to basal planes. In the presence of a chemical species, such as the Cl^- anion, with an ability to neutralize (reduce) the oxygen radicals and thus avert attack (oxidation) of the graphite anode, radical neutralization will effectively take place only if the concentration of this chemical species is sufficiently

high so that it can reach and neutralize the oxygen radical before the latter can attack the graphite anode. From this reasoning, it follows that the concentration of oxidation-preventing species required to avert attack by oxygen radicals will be higher in the case of graphite edges (faster attack by radicals) than in the case of basal planes (slower attack). Consequently, there should be a range of concentrations below a certain threshold for which oxidative attack is prevented in the basal plane but not at graphite edges. In this case, exfoliation of the graphite anode would be able to take place, giving rise to graphene products with a low extent of oxidation. This was indeed the case of NaCl and KCl at a concentration of 0.1 M. On the other hand, if the concentration of the oxidation-preventing agent in the electrolytic medium is sufficiently high, oxidative attack will also be arrested at the graphite edges, and hence we would expect no exfoliation of the graphite anode at all. As a matter of fact, this was the situation observed for NaCl and KCl at a concentration of 1 M.

Furthermore, we note that graphite foil could be anodically exfoliated using NaCl or KCl as the only electrolyte (i.e., in the absence of Na_2SO_4) [33]. However, in this case the delamination process was somewhat inefficient, yielding comparatively small amounts of graphene, which can be ascribed to a poor ability of the chloride anion to intercalate graphite on its own. Furthermore, exfoliation was possible just in a very narrow range of chloride concentrations (around 0.05 M, but not at 0.01 and 0.1 M) and the process was substantially less efficient in averting graphene oxidation (O/C ratio of the resulting graphene ~ 0.06). Hence, the use of NaCl or KCl as an additive (co-electrolyte) of a main electrolyte (Na_2SO_4) is clearly advantageous over their use as the only electrolyte for anodic exfoliation. We surmise that the sulfate anions act as a sort of advance party in the intercalation and exfoliation of the graphite anode, triggering the expansion of the interlayer space to a point where the subsequent entry of the oxidation-preventing chloride anions is greatly facilitated. Likewise, the use of commercial table salt (typically made up of 97-99 wt% NaCl plus some anticaking and other added agents as minor components) as an additive led to anodically exfoliated graphenes with the same characteristics as those of graphenes derived from the pure, analytical-grade NaCl. Particularly, high quality graphene with a very low degree of oxidation could be similarly attained with a proper concentration of table salt, i.e., 6 mg mL^{-1} (amounting to $\sim 0.1 \text{ M}$ of its NaCl component). Considering that up-scaling the production of electrochemically exfoliated graphene to the tonne scale is expected in the near future [34], the present results bode well for the industrial implementation of the anodic

approach towards high quality, low-oxidized graphene, as only very cheap and abundant source materials are required.

2.2. Further characterization of the low-oxidized anodic graphene

The improved structural quality of the anodic graphenes obtained using NaCl or KCl as an electrolyte additive was confirmed by their high resolution C 1s X-ray photoelectron spectra as well as by Raman spectroscopy. Fig. 2a shows the C 1s photoelectron spectrum of graphene prepared with 0.1 M NaCl additive (red trace). For comparison purposes, the spectra for the starting graphite foil (black trace) and the control sample (graphene exfoliated only with 0.1 M Na₂SO₄, orange trace) are also given. The survey spectra of these three samples are also presented in Fig. S2 of the ESM. In all cases, the C 1s envelope was dominated by a component centered at a binding energy of about 284.6 eV, corresponding to carbon atoms in unoxidized graphitic environments (sp²-based C=C species). Nonetheless, while the relatively oxidized control sample exhibited significant additional components in the 285-288 eV range, ascribed to carbon atoms in different oxidation states (C-O and C=O species) [7,11,20,29], such components were almost absent from the graphene sample obtained using the NaCl additive, as noticed by comparing its C 1s envelope with that of the starting graphite foil. This result further supports the conclusion that very few carbon atoms from the graphene lattice become oxidized during anodic exfoliation in the presence of proper amounts of chloride anions. Moreover, the water contact angle for paper-like graphene films (~20-25 μm thick) obtained through vacuum filtration of the NaCl-derived graphene nanosheets dispersed in water/isopropanol was determined to be 116±4° (inset to Fig. 2a), indicating that the material was hydrophobic as expected from its very low oxidation degree. Significantly, this contact angle was much larger than that of its counterpart prepared from graphene nanosheets anodically exfoliated in the absence of NaCl (60±8°; see Fig. S2 in the ESM). Such a result was consistent with the higher hydrophilicity expected for the latter graphene material on account of its substantially larger degree of oxidation relative to graphene prepared in the presence of NaCl as a co-electrolyte. On the other hand, the contact angle measured for the starting graphite foil (60±2°; Fig. S2 in the ESM) was virtually the same as that determined for the graphene film obtained in the absence of NaCl, even though we could have expected it to be more comparable to that of the graphene film obtained in the presence of NaCl due to their similar (very low) extent of oxidation. However, we note that the contact angle of the starting graphite foil cannot be directly compared to that of the anodically

exfoliated graphene films, because in addition to surface chemistry, the wettability of surfaces is also known to depend on their morphology/roughness. While the two graphene films can be expected to possess a similar surface morphology (they are made up of graphene nanosheets with similar lateral size and thickness, and assembled using the very same filtration method), the surface morphology of the starting graphite foil should be different, as it is made up of collections of much larger and thicker roll-pressed graphite particles.

The Raman spectra of graphene obtained with 0.1 M NaCl additive (red trace), starting graphite foil (black) and control sample (orange) are presented in Fig. 2b. Their first-order region (1100-1700 cm^{-1} range) incorporated the well-known G and defect-related D bands characteristic of graphite- and graphene-based materials [35,36], which were located at ~ 1582 and ~ 1350 cm^{-1} , respectively. An additional, weaker defect-related band (D' band) appeared in some cases as a shoulder on the high wavenumber side of the G band at ~ 1620 cm^{-1} . The second order region (2300-3300 cm^{-1}) was dominated by the 2D band (~ 2700 cm^{-1}). As a quantitative proxy of structural quality and defect density [36], the integrated intensity ratio of the D and G bands (I_D/I_G ratio) was used to reveal the possible introduction of structural imperfections in the graphene samples upon anodic exfoliation. The I_D/I_G ratio for graphene prepared with 0.1 M NaCl additive was determined to be 0.21 ± 0.06 , which was significantly smaller than that of the control sample (1.3 ± 0.2) and consistent with the higher structural quality expected for the former as a result of its lower extent of oxidation. By contrast, the I_D/I_G ratio for the starting graphite foil was a meager 0.03 ± 0.02 . Rather than arising from basal plane defects induced by oxidation, we infer that the significant increase in I_D/I_G ratio observed for the NaCl-derived graphene relative to the starting graphite stems mostly from the presence of a larger fraction of edges in the exfoliated nanosheets, which in turn can be ascribed to their relatively small (micrometric/submicrometric) size. Such a conclusion was supported by measurement of the $I_D/I_{D'}$ ratio, the magnitude of which has been proposed to reflect the type of prevailing defect in graphene materials [37,38]. Specifically, $I_D/I_{D'}$ values around 13, 7 and 3.5 have been associated to graphenes with imperfections dominated by basal plane sp^3 -defects, vacancy defects and boundaries/edges, respectively. $I_D/I_{D'}$ was calculated to be ~ 4.5 for the NaCl-derived graphene, thus suggesting that the increase in I_D/I_G ratio for such a sample relative to the starting graphite foil referred to above was largely due to the generation of exfoliated nanosheets with relatively small sizes (increased fraction of edges). Furthermore, when

using the measured I_D/I_G ratio to estimate the average lateral size of the graphene nanosheets ($\langle L \rangle$) by way of the formula recently proposed by Backes et al [39], which assumes the intensity of the D band to arise mostly from edges and not from basal plane defects, we obtained $\langle L \rangle$ values in the range between a few and several hundreds of nanometers. This result was in good agreement with the typical sizes of the nanosheets as imaged by scanning transmission electron microscopy (STEM; Fig. 2c) and atomic force microscopy (AFM; Fig. 2d). By contrast, the values of $\langle L \rangle$ derived from I_D/I_G for the control sample were substantially smaller (~ 50 - 100 nm), even though the actual size of the corresponding nanosheets was very similar to that of their NaCl-derived counterparts (images not shown). Hence, unlike the case of the latter, the nanosheets from the control sample were concluded to possess a significant amount of basal plane defects generated from the anodic delamination process, as could be anticipated on the basis of their substantial oxidation degree.

As illustrated by the line profiles from Fig. 2d, AFM was also used to assess the thickness of the exfoliated nanosheets deposited onto SiO_2/Si substrates. Apparent thickness values were determined to be typically between ~ 1.5 and 2.5 nm. Taking into account that this technique introduces a positive offset of ~ 1 nm in the measurement of graphene thickness, as is well known [40-42], we estimated the actual thickness of the nanosheets to be between ~ 0.5 and 1.5 nm. This result implies that such nanosheets were mostly single- to few-layered (< 5) objects, which in turn indicates that the efficiency of the anodic exfoliation process was not compromised by the use of NaCl as an electrolyte additive. The electrical conductivity (σ) of the paper-like, NaCl-derived graphene films was measured to further emphasize their high structural quality, yielding $\sigma \sim 34000 \text{ S m}^{-1}$. This figure was similar to, or even higher than, those previously reported for films of high quality, low-oxidized anodic graphene obtained with other oxidation-preventing electrolytes, such as sulfonated naphthalenes ($\sigma \sim 46000 \text{ S m}^{-1}$) [20], or electrolyte additives (e.g., TEMPO; $\sigma \sim 10000 \text{ S m}^{-1}$ [18]), and generally higher than those determined for as-prepared (without post-treatment) films of pristine graphene derived from direct, ultrasound- or shear-induced exfoliation in organic solvents ($\sigma \sim 5400$ - 20000 S m^{-1}) [38-44].

2.3. Applications of the low-oxidized anodic graphene in water/oil remediation and capacitive energy storage

A high quality, low-oxidized graphene produced in large amounts in powder form, like the one developed here by anodic exfoliation with NaCl as an electrolyte additive, could find practical use in water and oil remediation applications, where hydrophobic sorbents are typically required [45-47], and in electrochemical energy storage, where electrodes with a high electrical conductivity are needed [48-50]. Indeed, as discussed above, this graphene material was highly hydrophobic and electrically conductive. To explore such possibilities, we have examined its performance as an adsorbent of dyes from the aqueous phase and as a sorbent for oils and non-polar organic solvents, as well as an electrode for capacitive energy storage (see ESM for details on the experimental procedures). To this end, we used the as-exfoliated product (Fig. 1b), i.e., the material directly obtained from the anodic treatment (only washed with water and dried) that was not submitted to sonication in any solvent to separate individual graphene nanosheets from one another. Such a material was a fluffy, low density powder ($\sim 30\text{-}40\text{ mg cm}^{-3}$) that could be manipulated for the intended purposes more conveniently than the individual, solvent-dispersed nanosheets.

Fig. 3a shows the measured adsorption capacities of the graphene product towards five different dyes, namely, rose bengal, methylene green, basic fuchsin, methylene blue and methyl orange. The adsorption values ranged between $\sim 130\text{ mg g}^{-1}$ (for rose bengal) and $\sim 450\text{ mg g}^{-1}$ (for methyl orange). These figures were similar to, or even better than, those of many graphene-based adsorbents previously reported in the literature [45,51,52] (see Table S1 in the ESM for a detailed comparison of adsorption capacities). The good adsorption performance of the present graphene powder can be ascribed to its characteristic morphology consisting of very thin rippled sheets separated by micrometer- to nanometer-sized voids (Fig. 1d), which in turn should be associated to a large exposed surface area. Indeed, the dye adsorption capacities of the as-exfoliated graphene following a sonication step, whereby many individual graphene nanosheets are physically detached from the bulk powder, were not very different to those determined before sonication, thus suggesting that the surface area available for dye adsorption was already well developed in the as-exfoliated (non-sonicated) material. Concerning the sorption of oils and non-polar organic solvents, the measured capacities were typically between $15\text{ and }30\text{ g g}^{-1}$ (Fig. 3b). Even though these values were relatively modest compared to those obtained with very lightweight graphene-based sorbents [45,47] (a detailed comparison of different sorbents is given in Table S2 of the ESM), they were nonetheless consistent with what could be expected for a

material with a density of 30-40 mg cm⁻³. Moreover, very lightweight graphene-based sorbents are commonly obtained through the production and processing of graphite oxide, which in turn involves time-consuming and relatively complicated procedures [46,47]. By contrast, the anodic graphene material investigated here can be prepared in a short time by a very simple process, thus making its use particularly attractive from an applied perspective.

The results of testing the low-oxidized anodic graphene as an electrode for capacitive energy storage are presented in Fig. 3c-f. The measurements were carried out in a three-electrode configuration, using a commercial activated carbon as a counter electrode and Ag/AgCl (3 M KCl) as a reference electrode (see ESM for details). Fig. 3c shows the cyclic voltammogram of the graphene electrode recorded at a potential scan rate of 3 mV s⁻¹. Even at such a low scan rate, the voltammogram exhibited a nearly rectangular shape with no significant redox peaks (except for some slight oxidation/reduction humps at ~0.4-0.5 V vs Ag/AgCl), indicating that charge storage in the electrode was mostly dominated by the formation of an electric double layer with little contribution from Faradaic processes (i.e., pseudocapacitance). This observation was in agreement with the very limited amount of oxygen functional groups (and indeed of any other heteroatoms) detected by XPS for this graphene sample, the presence of which is generally ascribed to the emergence of pseudocapacitance in carbon materials [48,49]. Furthermore, the rectangular shape of the voltammograms was largely retained upon increasing the voltage scan rate (Fig. 3d), although some degree of distortion became apparent at the highest rates (i.e., 300 and 500 mV s⁻¹). The latter would indicate that access of the electrolyte ions to certain areas of the electrode is somewhat sluggish, which in turn could be due to the particular morphology of the graphene product that is obtained from the anodic process. More specifically, the FE-SEM images of the anodically expanded material (e.g., Fig. 1d) suggest that there could be very narrow voids between parallel sheets at some specific points, creating two-dimensional slit pores where ion adsorption/desorption can take place. Because the anodic treatment does not lead on its own to a complete separation of the graphene layers, we can expect many of these two-dimensional voids to be closed at one of their ends, thus creating cul-de-sac porosities that hamper ionic transport to/from these pores.

Typical galvanostatic charge/discharge curves recorded at different current densities between 0.05 and 10 A g⁻¹ are presented in Fig. 3e. The curves displayed mostly triangular and symmetrical shapes, this being again consistent with capacitive

processes as the main driving force behind charge storage in the graphene electrode. As shown in Fig. 3f, the gravimetric capacitance values derived from the discharge curves were highest (around 120 F g^{-1}) at the lowest current densities and decreased down to $\sim 50 \text{ F g}^{-1}$ at a current density of 10 A g^{-1} . These figures lay within the range of values measured for many graphene-based materials that have previously tested as electrodes for capacitive energy storage [48,50] (see Table S3 in the ESM for a comparative list). However, different to the case of these prior graphene materials, many of which were obtained through complex preparation and processing steps (e.g., via the graphite oxide route, or by chemical vapor deposition for very high quality graphenes), a practical advantage of the present approach was its simplicity of operation and the use of inexpensive, environmentally friendly and widely available reagents. Moreover, the stability of the graphene electrode was demonstrated by noting that about 98% of its initial capacitance could be retained after 10000 consecutive charge/discharge cycles at 2 A g^{-1} (inset to Fig. 3f).

3. Conclusions

We have demonstrated the production of high quality and low-oxidized graphene nanosheets by anodic exfoliation of graphite in water using NaCl (table salt) as an electrolyte additive (co-electrolyte) with a remarkable efficiency in preventing the oxidation of the nanosheets that is commonly associated to such a process. Different to previous instances, where relatively complex and expensive electrolyte additives were employed to avert the oxidation of anodically exfoliated graphene, the present work has introduced a particularly cheap, straightforward and readily available substance as an alternative oxidation-preventing co-electrolyte. The high efficiency of this additive in curtailing oxidative attack of the exfoliated nanosheets was particularly significant, yielding anodic graphene with the lowest extent of oxidation reported to date (O/C ratio ~ 0.02 - 0.03). The as-prepared, low-oxidized graphene material also demonstrated its potential practical utility as a sorbent of dyes and non-polar organic solvents for water/oil remediation processes, as well as an electrode for capacitive energy storage, its simplicity of preparation and processing being an additional asset compared to other graphene-based materials. Finally, because only inexpensive raw materials that are available in large quantities were required for its production, we believe the anodic route is now better positioned as a competitive approach in the efforts to industrialize the manufacturing of high quality graphene for different applications.

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References

- [1] A.C. Ferrari, F. Bonaccorso, V. Fal'ko, K. S. Novoselov, S. Roche, P. Boggild, S. Borini, F. H. L. Koppens, V. Palermo, N. Pugno, J. A. Garrido, R. Sordan, A. Bianco, L. Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhanen, A. Morpurgo, J. N. Coleman, V. Nicolosi, L. Colombo, A. Fert, M. Garcia-Hernandez, A. Bachtold, G. F. Schneider, F. Guinea, C. Dekker, M. Barbone, Z. Sun, C. Galiotis, A. N. Grigorenko, G. Konstantatos, A. Kis, M. Katsnelson, L. Vandersypen, A. Loiseau, V. Morandi, D. Neumaier, E. Treossi, V. Pellegrini, M. Polini, A. Tredicucci, G. M. Williams, B. Hee Hong, J.-H. Ahn, J. Min Kim, H. Zirath, B. J. van Wees, H. van der Zant, L. Occhipinti, A. Di Matteo, I. A. Kinloch, T. Seyller, E. Quesnel, X. Feng, K. Teo, N. Rupesinghe, P. Hakonen, S. R. T. Neil, Q. Tannock, T. Lofwander, J. Kinaret, Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems, *Nanoscale* 7 (2015), 4598-4810.
- [2] H.J. Salavagione, Promising alternative routes for graphene production and functionalization, *J. Mater. Chem. A* 2 (2014), 7138-7146.
- [3] A.M. Abdelkader, A.J. Cooper, R.A.W. Dryfe, I.A. Kinloch, How to get between the sheets: a review of recent works on the electrochemical exfoliation of graphene materials from bulk graphite, *Nanoscale* 7 (2015), 6944-6956.
- [4] S. Yang, M.R. Lohe, K. Müllen, X. Feng, New-generation graphene from electrochemical approaches: production and applications, *Adv. Mater.* 28 (2016), 6213-6221.

- [5] Y.L. Zhong, Z. Tian, G.P. Simon, D. Li, Scalable production of graphene via wet chemistry: progress and challenges, *Mater. Today* 18 (2015), 73-78.
- [6] A.T. Najafabadi, E. Gyenge, Synergistic production of graphene microsheets by simultaneous anodic and cathodic electro-exfoliation of graphitic electrodes in aprotic ionic liquids, *Carbon* 84 (2015), 449-459.
- [7] S. Yang, A.G. Ricciardulli, S. Liu, R. Dong, M.R. Lohe, A. Becker, M.A. Squillaci, P. Samorì, K. Müllen, X. Feng, Ultrafast delamination of graphite into high-quality graphene using alternating currents, *Angew. Chem. Int. Ed.* 56 (2017), 6669-6675.
- [8] A.J. Cooper, N.R. Wilson, I.A. Kinloch, R.A.W. Dryfe, Single stage electrochemical exfoliation method for the production of few-layer graphene via intercalation of tetraalkylammonium cations, *Carbon* 66 (2014), 340-350.
- [9] M. Zhao, X.-Y. Guo, O. Ambacher, C.E. Nebel, R. Hoffmann, Electrochemical generation of hydrogenated graphene flakes, *Carbon* 83 (2015), 128-135.
- [10] Y.R. Leroux, J.-F. Bergamini, S. Ababou, J.-C. Le Breton, P. Hapiot, Synthesis of functionalized few-layer graphene through fast electrochemical expansion of graphite, *J. Electroanal. Chem.* 753 (2015), 42-46.
- [11] J. Liu, M. Notarianni, G. Will, V.T. Tiong, H. Wang, N. Motta, Electrochemically exfoliated graphene for electrode films: effect of graphene flake thickness on the sheet resistance and capacitive properties, *Langmuir* 29 (2013), 13307-13314.
- [12] L. Wu, W. Li, P. Li, S. Liao, S. Qiu, M. Chen, Y. Guo, Q. Li, C. Zhu, L. Liu, Powder, paper and foam of few-layer graphene prepared in high yield by electrochemical intercalation exfoliation of expanded graphite, *Small* 10 (2014), 1421-1429.
- [13] A. Ambrosi, M. Pumera, Electrochemically exfoliated graphene and graphene oxide for energy storage and electrochemistry applications, *Chem. Eur. J.* 22 (2016), 153-159.
- [14] Z. Liu, Z.-S. Wu, S. Yang, R. Dong, X. Feng, K. Müllen, Ultraflexible in-plane micro-supercapacitors by direct printing of solution-processable electrochemically exfoliated graphene, *Adv. Mater.* 28 (2016), 2217-2222.
- [15] P. Khanra, T. Kuila, S. H. Bae, N. H. Kim, J. H. Lee, Electrochemically exfoliated graphene using 9-anthracene carboxylic acid for supercapacitor application, *J. Mater. Chem.* 22 (2012) 24403-24410.

- [16] P. Khanra, C.-N. Lee, T. Kuila, N. H. Kim, M. J. Park, J. H. Lee, 7,7,8,8-Tetracyanoquinodimethane-assisted one step electrochemical exfoliation of graphite and its performance as an electrode material, *Nanoscale* 6 (2014) 4864–4873.
- [17] J.I. Paredes, J.M. Munuera, Recent advances and energy-related applications of high quality/chemically doped graphenes obtained by electrochemical exfoliation methods, *J. Mater. Chem. A* 5 (2017), 7228-7242.
- [18] S. Yang, S. Brüller, Z.-S. Wu, Z. Liu, K. Parvez, R. Dong, F. Richard, P. Samorì, X. Feng, K. Müllen, Organic radical-assisted electrochemical exfoliation for the scalable production of high-quality graphene, *J. Am. Chem. Soc.* 137 (2015), 13927-13932.
- [19] C.-H. Chen, S.-W. Yang, M.-C. Chuang, W.-Y. Woon, C.-Y. Su, Towards the continuous production of high crystallinity graphene via electrochemical exfoliation with molecular in situ encapsulation, *Nanoscale* 7 (2015), 15362-15373.
- [20] J.M. Munuera, J.I. Paredes, S. Villar-Rodil, M. Ayán-Varela, A. Martínez-Alonso, J.M.D. Tascón, Electrolytic exfoliation of graphite in water with multifunctional electrolytes: en route towards high quality, oxide-free graphene flakes, *Nanoscale* 8 (2016), 2982-2998.
- [21] K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Müllen, Exfoliation of graphite into graphene in aqueous solutions of inorganic salts, *J. Am. Chem. Soc.* 136 (2014), 6083-6091.
- [22] S.C. Foote, J.S. Valentine, A. Greenberg, J.F. Liebman, *Active Oxygen in Chemistry*, Chapman & Hall, Glasgow, 1995.
- [23] P. Vanýsek, *CRC handbook of Chemistry and Physics*, 93rd edition, CRC Press, Boca Raton, 2012.
- [24] G.G. Jayson, B.J. Parsons, A.J. Swallow, Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. Their formation using pulses of radiation and their role in the mechanism of the Fricke dosimeter, *J. Chem. Soc., Faraday Trans. 1* 69 (1973), 1597-1607.
- [25] L.B. Ebert, *Annu. Intercalation compounds of graphite*, *Rev. Mater. Sci.* 6 (1976), 181-211.
- [26] H. Shioyama, R. Fujii, Electrochemical reactions of stage 1 sulfuric acid—Graphite intercalation compound, *Carbon* 25 (1987), 771-774.

- [27] C.-Y. Su, A.-Y. Lu, Y. Xu, F.-R. Chen, A.N. Khlobystov, L.-J. Li, High-quality thin graphene films from fast electrochemical exfoliation, *ACS Nano* 5 (2011), 2332-2339.
- [28] J.M. Munuera, J.I. Paredes, S. Villar-Rodil, A. Martínez-Alonso, J.M.D. Tascón, A simple strategy to improve the yield of graphene nanosheets in the anodic exfoliation of graphite foil, *Carbon* 115 (2017), 628-632.
- [29] J.M. Munuera, J.I. Paredes, S. Villar-Rodil, M. Ayán-Varela, A. Pagán, S.D. Aznar-Cervantes, J.L. Cenis, A. Martínez-Alonso, J.M.D. Tascón, High quality, low oxygen content and biocompatible graphene nanosheets obtained by anodic exfoliation of different graphite types, *Carbon* 94 (2015), 729-739.
- [30] D. Li, M.B. Müller, S. Gilje, R.B. Kaner, G.G. Wallace, Processable aqueous dispersions of graphene nanosheets, *Nat. Nanotechnol.* 3 (2008), 101-105.
- [31] L. Guardia, M.J. Fernández-Merino, J.I. Paredes, P. Solís-Fernández, S. Villar-Rodil, A. Martínez-Alonso, J.M.D. Tascón, High-throughput production of pristine graphene in an aqueous dispersion assisted by non-ionic surfactants, *Carbon* 49 (2011), 1653-1662.
- [32] J.I. Paredes, A. Martínez-Alonso, J.M.D. Tascón, Multiscale imaging and tip-scratch studies reveal insight into the plasma oxidation of graphite, *Langmuir* 23 (2007), 8932-8943.
- [33] J.M. Munuera, J.I. Paredes, M. Enterría, A. Pagán, S. Villar-Rodil, M.F.R. Pereira, J.I. Martins, J.L. Figueiredo, J.L. Cenis, A. Martínez-Alonso, J.M.D. Tascón, Electrochemical exfoliation of graphite in aqueous sodium halide electrolytes toward low oxygen content graphene for energy and environmental applications, *ACS Appl. Mater. Interfaces* 9 (2017), 24085-24099.
- [34] X.-Y. Wang, A. Narita, K. Müllen, Precision synthesis versus bulk-scale fabrication of graphenes, *Nat. Rev. Chem.* 2 (2017), 00100.
- [35] M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, L.G. Cançado, A. Jorio, R. Saito, Studying disorder in graphite-based systems by Raman spectroscopy, *Phys. Chem. Chem. Phys.* 9 (2007), 1276-1291.
- [36] A.C. Ferrari, D.M. Basko, Raman spectroscopy as a versatile tool for studying the properties of graphene, *Nat. Nanotechnol.* 8 (2013), 235-246.

- [37] A. Eckmann, A. Felten, A. Mishchenko, L. Britnell, R. Krupke, K.S. Novoselov, C. Casiraghi, Probing the nature of defects in graphene by Raman spectroscopy, *Nano Lett.* 12 (2012), 3925-3930.
- [38] K. R. Paton, E. Varrla, C. Backes, R. J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O. M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S. E. O'Brien, E. K. McGuire, B. Mendoza Sanchez, G. S. Duesberg, N. McEvoy, T. J. Pennycook, C. Downing, A. Crossley, V. Nicolosi, J. N. Coleman, Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids, *Nat. Mater.* 13 (2014), 624–630.
- [39] C. Backes, K.R. Paton, D. Hanlon, S. Yuan, M.I. Katsnelson, J. Houston, R.J. Smith, D. McCloskey, J.F. Donegan, J.N. Coleman, Spectroscopic metrics allow in situ measurement of mean size and thickness of liquid-exfoliated few-layer graphene nanosheets, *Nanoscale* 8 (2016), 4311-4323.
- [40] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, *Science* 306 (2004), 666-669.
- [41] P. Nemes-Incze, Z. Osváth, K. Kamarás, L.P. Biró, Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy, *Carbon* 46 (2008), 1435-1442.
- [42] P. Solís-Fernández, J.I. Paredes, S. Villar-Rodil, A. Martínez-Alonso, J.M.D. Tascón, Determining the thickness of chemically modified graphenes by scanning probe microscopy, *Carbon* 48 (2010), 2657-2660.
- [43] U. Khan, A. O'Neill, M. Lotya, S. De, J.N. Coleman, High-concentration solvent exfoliation of graphene, *Small* 6 (2010), 864-871.
- [44] K.H. Park, B.H. Kim, S.H. Song, J. Kwon, B.S. Kong, K. Kang, S. Jeon, Exfoliation of non-oxidized graphene flakes for scalable conductive film, *Nano Lett.* 12 (2012), 2871-2876.
- [45] Z. Niu, L. Liu, L. Zhang, X. Chen, Porous graphene materials for water remediation, *Small* 10 (2014), 3434-3441.
- [46] B. Chen, Q. Ma, C. Tan, T.-T. Lim, L. Huang, H. Zhang, Carbon-based sorbents with three-dimensional architectures for water remediation, *Small* 11 (2015), 3319-3336.

- [47] W. Wan, Y. Lin, A. Prakash, Y. Zhou, Three-dimensional carbon-based architectures for oil remediation: from synthesis and modification to functionalization, *J. Mater. Chem. A* 4 (2016), 18687-18705.
- [48] J. Chen, C. Li, G. Shi, Graphene materials for electrochemical capacitors, *J. Phys. Chem. Lett.* 4 (2013), 1244-1253.
- [49] R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, The role of graphene for electrochemical energy storage, *Nat. Mater.* 14 (2015), 271-279.
- [50] H. Wu, Y. Zhang, L. Cheng, L. Zheng, Y. Li, W. Yuan, X. Yuan, Graphene based architectures for electrochemical capacitors, *Energy Stor. Mater.* 5 (2016), 8-32.
- [51] F. Li, X. Jiang, J. Zhao, S. Zhang, Graphene oxide: A promising nanomaterial for energy and environmental applications, *Nano Energy* 16 (2015), 488-515.
- [52] H. Wang, X. Yuan, G. Zeng, Y. Wu, Y. Liu, Q. Jiang, S. Gu, Three dimensional graphene based materials: Synthesis and applications from energy storage and conversion to electrochemical sensor and environmental remediation, *Adv. Colloid Interface Sci.* 221 (2015), 41-59.

Table 1. O/C atomic ratios determined from XPS data for anodic graphene obtained in the presence of 0.1 M Na₂SO₄ as the main electrolyte and different molar concentrations of a second compound used as an additive (co-electrolyte).

Electrolyte additive	Concentration (M)	O/C ratio
None	0.00	0.09
NaCl	0.01	0.24
	0.05	0.05
	0.10	0.03
	0.20	0.03
	0.50	0.03
KCl	0.01	0.13
	0.05	0.02
	0.10	0.04
	0.25	0.02
NaBr	0.01	0.19
	0.10	0.11
NaI	0.01	0.16
	0.10	0.13
Na₂SO₃	0.01	0.19
	0.10	0.12
Sodium citrate	0.01	0.14
	0.10	0.05
Sodium ascorbate	0.01	0.12
NaBH₄	0.01	0.16
Ethanol	1.7	0.20
	4.3	0.21
	17.3	0.24
	35.0	0.23
	44.0	0.24
	53.0	0.09
	71.5	0.06

Figure 1. (a) Schematic of the anodic exfoliation of graphite using different compounds as additives (co-electrolytes) of Na_2SO_4 (main electrolyte) in the potential role of oxidation-preventing agents. (b-d) Digital photograph (b) as well as low (c) and high (d) magnification FE-SEM images of the as-prepared graphene product obtained with NaCl as a co-electrolyte with scale bars of 1 mm (c) and 20 μm (d). (e) Digital photograph of graphene obtained with NaCl as a co-electrolyte and colloidally dispersed in water/isopropanol mixture (left cuvette), *N,N*-dimethylformamide (center) and water with flavin mononucleotide stabilizer (right) after mild sonication of the as-prepared material. (f) UV-vis optical absorption spectrum of the graphene dispersion in water/isopropanol mixture.

Figure 2. (a,b) High resolution C 1s core-level spectra (a) and Raman spectra (b) of the starting graphite foil (black trace), graphene anodically exfoliated in 0.1 M Na₂SO₄ electrolyte (orange trace) and graphene anodically exfoliated in 0.1 M Na₂SO₄ with 0.1 M NaCl as a co-electrolyte (red trace). Inset to a: digital photograph of a water droplet (~2 μL) deposited onto a vacuum-filtered film of graphene prepared by anodic exfoliation in the presence of NaCl co-electrolyte. (c,d) STEM (c) and AFM (d) images of graphene nanosheets produced by anodic exfoliation with NaCl co-electrolyte. A typical line profile of a nanosheet taken along the marked white line is shown overlaid on the AFM image.

Figure 3. Applications of the as-prepared, low-oxidized anodic graphene obtained with NaCl as a co-electrolyte. (a,b) Histograms showing the adsorption capacity of the material towards different dyes in aqueous solution (a) as well as its sorption capacity towards different oils and non-polar organic solvents (b). (c) Cyclic voltammogram recorded at a potential scan rate of 3 mV s^{-1} . (d) Cyclic voltammograms recorded at potential scan rates between 3 and 500 mV s^{-1} . (e) Galvanostatic charge/discharge curves recorded at different current densities between 0.05 and 10 A g^{-1} . (f) Gravimetric capacitance values determined at different current densities from the discharge curves in e. Inset to f: evolution of capacitance values (in percentage) of the electrode measured at a current density of 2 A g^{-1} for consecutive charge/discharge cycles (up to 10000).

Electronic Supplementary Material for

High quality, low-oxidized graphene via anodic exfoliation with table salt as an efficient oxidation-preventing co-electrolyte for water/oil remediation and capacitive energy storage applications

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S1. Electrochemical exfoliation experiments

Unless otherwise stated, all the materials and chemicals used throughout this study were obtained from Sigma-Aldrich. Milli-Q deionized water (Millipore Corporation; resistivity: 18.2 M Ω ·cm) was employed in all the experiments. The electrochemical (anodic) exfoliation experiments were carried out in a two-electrode setup consisting of a high purity graphite foil piece (Papyex I980, acquired from Mersen; dimensions: $\sim 40 \times 25 \times 0.5$ mm³) as the working electrode and a platinum foil (thickness: 0.025 mm) as the counter electrode. Both electrodes were immersed in an aqueous electrolyte solution (80 mL) incorporating 0.1 M Na₂SO₄ as the main electrolyte and a given molar concentration of another chemical species as the electrolyte additive. Although best results in terms of preventing oxidation of the exfoliated graphene nanosheets were obtained with NaCl, other electrolyte additives tested included KCl, KBr, KI, NaBH₄, Na₂SO₃, sodium citrate, vitamin C and ethanol. To trigger its delamination, a positive voltage (10 V) was applied to the graphite foil electrode for 60 min by means of an Agilent 6614C DC power supply, while keeping the platinum counter electrode parallel to the graphite foil surface at a distance of about 2 cm. During the electrolytic process the outer layers of the graphite electrode were seen to swell and expand, giving rise to many millimeter-sized fragments that detached from the electrode and tended to float on the aqueous solution. Subsequently, these fragments as well as the swollen graphitic material that had not yet detached from the electrode (retrieved by gently scraping with a spatula) were collected, rinsed off with copious amounts of water through filter paper and dried overnight at room temperature under reduced pressure. The resulting product was transferred either to a water/isopropanol mixture (65/35 v/v%), to an aqueous solution of the dispersant flavin mononucleotide (FMN, 1 mg mL⁻¹) or to the organic solvent *N,N*-dimethylformamide (DMF), sonicated in an ultrasound bath cleaner (J.P. Selecta Ultrasons system, 40 kHz) for 3 h and finally centrifuged at 200 g for 20 min (Eppendorf 5424 microcentrifuge) to obtain a colloidal suspension (supernatant) of graphene nanosheets in these solvents.

S2. Characterization techniques

The obtained materials were characterized by field emission scanning electron microscopy (FE-SEM), scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), UV-vis absorption spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and measurement of electrical conductivity and water contact angle. FE-SEM and STEM images were recorded in a Quanta FEG 650 microscope (FEI Company) at 25 kV. Specimens for STEM were prepared by drop-casting ~40 μL of graphene dispersed in water/isopropanol onto copper grids (200 mesh) covered with a thin continuous film of amorphous carbon. AFM imaging of the graphene nanosheets was performed in the tapping mode of operation with a Nanoscope IIIa Multimode apparatus (Veeco Instruments), using rectangular silicon cantilevers (spring constant: ~40 N m^{-1} ; resonance frequency: 250-300 kHz). To this end, the nanosheets were deposited onto pre-heated (~50-60 $^{\circ}\text{C}$) highly oriented pyrolytic graphite (HOPG) substrates by drop-casting their colloidal dispersion in water/isopropanol. UV-vis absorption spectroscopy was accomplished in a double-beam He λ ios α spectrophotometer (Thermo Spectronic). Raman spectra were acquired in a Horiba Jobin-Yvon LabRam instrument at a laser excitation wavelength and incident power of 532 nm and 2 mW, respectively. XPS was carried out on a SPECS apparatus under a pressure of 10^{-7} Pa using a non-monochromatic Al K_{α} X-ray source (11.81 kV, 100 W). Specimens for both Raman spectroscopy and XPS were prepared by drop-casting graphene dispersions in water/isopropanol onto pre-heated (~50-60 $^{\circ}\text{C}$) stainless steel disks 12 mm in diameter until a thin, continuous graphene film with a lustrous gray tone became visible to the naked eye. The electrical conductivity of paper-like graphene films was measured on the basis of the van der Pauw method using a home-made setup consisting of an Agilent 6614C DC power supply and a Fluke 45 digital multimeter. The graphene films were prepared by vacuum filtration of graphene dispersions in water/isopropanol through polycarbonate membrane filters (Whatman; diameter: 25 mm; pore size: 0.2 μm) and were cut into $12 \times 12 \text{ mm}^2$ square pieces for the measurements, with their thickness being estimated by both FE-SEM and a high precision electronic caliper (Digimatic Micrometer, model MDC-25PX, from Mitutoyo). Measurement of water contact angles was carried out on the paper-like graphene films by carefully dropping 2 μL of water on the films with a pipette and immediately taking images of the droplet using a standard digital camera attached with

a macro lens. Contact angles were determined from the recorded images through analysis with ImageJ software.

S3. Applications of the high quality, anodically exfoliated graphene

To explore their possible applications, the high quality graphene materials developed in this work were tested as adsorbents for water-soluble dyes and as sorbents for non-polar organic solvents and dyes, as well as electrodes for capacitive energy storage. In this case, the as-exfoliated graphene materials, i.e., the products directly obtained from the anodic delamination process without a subsequent sonication step (only washed with water to remove remnants of the electrolyte) were used, as they exhibited a powdery, three-dimensional morphology that was convenient for their manipulation. The dye adsorption tests were carried out by adding ~1.5 mg of graphene material to 1.5 mL of an aqueous solution of a given dye at room temperature and pH ~6, followed by gently stirring with a magnetic bar for 24 h to ensure the attainment of adsorption equilibrium and centrifuging the solution (20000 g, 20 min) to sediment the graphene component. The concentration of the dye in the resulting supernatant was then determined by means of UV-vis absorption spectroscopy and contrasted with that of the starting dye solution, which in turn allowed the amount of dye adsorbed on the graphene sample to be estimated. The adsorption experiments were performed with the following dyes (wavelengths given in parenthesis correspond to the position of the absorption peak used to measure the dye concentration): methyl orange (460 nm), methylene blue (660 nm), basic fuchsin (540 nm), methylene green (660 nm) and rose bengal (560 nm). To determine the maximum adsorption capacities of the graphene materials, different starting concentrations of the dye (typically up to 2-3 mg mL⁻¹) were probed in the tests. For the sorption of oils and non-polar solvents, a certain mass of graphene material (typically ~5 mg) was first put into a 1.5 mL centrifuge tube. Then, small known volumes of a given oil/solvent (usually around 100 µL) were successively added to the tube. Such volumes were readily taken up by the graphene sample until a point was reached where the latter became saturated, which in turn allowed to estimate the total volume of oil/solvent retained by the sorbent. Sorption tests were conducted with the following substances: toluene, hexane, dodecane, tetrahydrofuran, acetone, chloroform, ethylene glycol, ethanol, olive oil, as well as unused and used pump oil.

Testing of the high quality anodic graphene as an electrode for capacitive energy storage was accomplished in a three-electrode configuration with a Swagelok-type cell, using a paste based on a commercial activated carbon (ACF A20) as the counter electrode and Ag/AgCl (3M KCl) as the reference electrode in an acidic aqueous electrolyte (1 M H₂SO₄). The counter electrode paste consisted of a mixture of the activated carbon, polytetrafluoroethylene (PTFE) as a binder and carbon black as a conductive additive in a weight ratio of 90:5:5. The graphene working electrode was prepared by pressing the as-prepared anodic graphene under a moderate force (1 ton for 15 s) onto a graphite foil support by means of a hydraulic press. Two pieces of glass microfiber filter (grade 934-AH, from Whatman) were used as the separator. Prior to assembling the cell, the working electrode, counter electrode and separator were soaked in the electrolyte and vacuum-degassed. The assembled cell with the electrolyte was also vacuum-degassed before the measurements, which were conducted in a Biologic VSP potentiostat. Both cyclic voltammograms at different potential scan rates and galvanostatic charge/discharge curves at different current densities were recorded.

S4. Additional figures

Figure S1. XPS survey spectra of the starting graphite foil (black trace), graphene anodically exfoliated in 0.1 M Na₂SO₄ electrolyte (orange trace) and graphene anodically exfoliated in 0.1 M Na₂SO₄ with 0.1 M NaCl as a co-electrolyte (red trace).

Figure S2. Digital photographs of water droplets (1–2 μ L) deposited onto the starting graphite foil (a), and vacuum-filtered films of graphene prepared by anodic exfoliation in the absence (b) and presence (c) of 0.1 M NaCl as a co-electrolyte.

S5. Additional tables

Table S1. Adsorption capacities of different dyes (methyl orange, methylene blue, methylene green, basic fuchsin and rose bengal) with a range of graphene-based materials.

Material	Adsorbate	Adsorption capacity (mg g ⁻¹)	Ref.
Graphene oxide	Methyl Orange	17	S1
CoFe2O4 functionalized graphene	Methyl orange	72	S2
Graphene oxide/Ni-Al LDH	Methyl orange	84	S3
Graphene oxide/Ni-Cr LDH	Methyl orange	160	S4
Graphene oxide/chitosan	Methyl orange	567	S5
As-prepared anodic graphene	Methyl orange	457	This work
Reduced graphene oxide	Methylene blue	154	S6
Graphene oxide	Methylene blue	244	S7
Citric acid functionalized magnetic graphene oxide	Methylene blue	316	S8
Agar/graphene oxide composite aerogel	Methylene blue	578	S9
Porous graphene oxide/hydrogel nanocomposite	Methylene blue	714	S10
As-prepared anodic graphene	Methylene blue	415	This work
As-prepared anodic graphene	Methylene green	343	This work
Reduced graphene oxide	Basic fuchsin	34	S11
β-cyclodextrin–carboxymethyl cellulose–graphene oxide composite	Basic fuchsin	59	S12
Reduced graphene oxide/ PSSMA	Basic fuchsin	388	S13
Graphene/β-cyclodextrin composite	Basic fuchsin	426	S14
Graphene oxide/polyacrylamide	Basic fuchsin	1034	S15
As-prepared anodic graphene	Basic fuchsin	361	This work
Graphene oxide/sodium alginate/polyacrylamide hydrogel	Rose Bengal	6	S16
Graphene Oxide@PLA@HA Composite	Rose Bengal	53	S17

Microcapsule			
Graphene sheets/graphene quantum dots	Rose Bengal	587	S18
As-prepared anodic graphene	Rose Bengal	130	This work

Table S2. Range of sorption capacities of different graphene-based materials towards oils and non-polar organic solvents.

Material	Retention capacity (g/g)	Ref.
Magnetic graphene foam	7-27	S19
Hydrothermal graphene sponge	20-35	S20
Graphene-carbon nanotube aerogel	20-35	S21
GO foam	5-40	S22
N-doped graphene aerogel	40-110	S23
Graphene sponge	80-160	S24
As-prepared anodic graphene	15-30	This work

Table S3. Gravimetric capacitance values of a range of graphene-based materials determined at different current densities.

Material	Current density (A/g)	Capacity (F/g)	Ref
rGO	0.3	57	S25
rGO/carbon black	1	79	S26
rGO	0.5	82	S27
rGO	1	116	S28
rGO foam	5	125	S29
rGO	1	130	S30
graphene hydrogel	1	186	S31
graphene/PANI nanofibers	0.3	210	S25
Highly crumpled N-doped graphene nanosheets	1	246	S32
Anodic graphene	0.3	105	This work
Anodic graphene	0.5	100	This work
Anodic graphene	1	94	This work
Anodic graphene	5	63	This work

S6. References

- [S1] D. Robatia, B. Mirzab, M. Rajabic, O. Moradid, I. Tyagie, S. Agarwaleg, V. K. Gupta, Removal of hazardous dyes-BR 12 and methyl orange using graphene oxide as an adsorbent from aqueous phase, *Chem. Eng. J.* 284 (2016) 687-697.
- [S2] N. Li, M. Zheng, X. Chang, G. Ji, H. Lu, L. Xue, L. Pan, J. Cao, Preparation of magnetic CoFe₂O₄-functionalized graphene sheets via a facile hydrothermal method and their adsorption properties, *J. Solid State Chem.* 184 (2011) 953-958.
- [S3] Z. Yang, S. Ji, W. Gao, C. Zhang, L. Ren, W. W. Tjiu, Z. Zhang, J. Pan, T. Liu, Magnetic Nanomaterial Derived from Graphene Oxide/Layered Double Hydroxide Hybrid for Efficient Removal of Methyl Orange from Aqueous Solution, *J. Colloid Interface Sci.* 408 (2013) 25-32.
- [S4] X. Ruan, Y. Chen, H. Chen, G. Qian, R. L. Frost, Sorption Behavior of Methyl Orange from Aqueous Solution on Organic Matter and Reduced Graphene Oxides Modified Ni–Cr Layered Double Hydroxides, *Chem. Eng. J.* 297 (2016) 295-303.
- [S5] Y. Wang, X. Liu, H. Wang, G. Xia, W. Huang, R. Song, Microporous Spongy Chitosan Monoliths Doped with Graphene Oxide as Highly Effective Adsorbent for Methyl Orange and Copper Nitrate (Cu(NO₃)₂) Ions, *J. Colloid Interface Sci.* 416 (2014) 243-251.
- [S6] T. Liu, Y. Lia, Q. Du, J. Sun, Y. Jiao, G. Yang, Z. Wang, Y. Xia, W. Zhang, K. Wang, H. Zhu, D. Wu, Adsorption of methylene blue from aqueous solution by graphene, *Colloids Surf. B* 90 (2012) 197-203.
- [S7] Y. Li, Q. Du, T. Liu, X. Peng, J. Wang, J. Sun, Y. Wang, S. Wu, Z. Wang, Y. Xia, L. Xia Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes, *Chem. Eng. Res. Des.* 91 (2013) 361-368.

- [S8] H. Ge, C. Wang, S. Liu, Z. Huang, Synthesis of citric acid functionalized magnetic graphene oxide coated corn straw for methylene blue adsorption, *Bioresour. Technol.* 221 (2016) 419-429.
- [S9] L.Chen, Y. Li, Q. Du, Z. Wang, Y. Xia, E. Yedinak, J. Lou, L. Ci, High performance agar/graphene oxide composite aerogel for methylene blue removal, *Carbohydr. Polym.* 155 (2017) 345-353.
- [S10] A. Pourjavadi, M. Nazari, B. Kabiri, S. H. Hosseini, C Bennett, Preparation of porous graphene oxide/hydrogel nanocomposites and their ability for efficient adsorption of methylene blue, *RSC Adv.* 6 (2016) 10430-10437.
- [S11] Ş.Tokaliolu, E. Yavuz, A. Aslantaş, H. Şahan, F. Taşkin, Ş. Patat, Spectrophotometric Determination of Basic Fuchsin from Various Water Samples after Vortex Assisted Solid Phase Extraction Using Reduced Graphene Oxide as an Adsorbent, *Spectrochim. Acta A* 149 (2015) 378-384.
- [S12] J. Yuan, F. Qiu, P. Li, Synthesis and characterization of β -cyclodextrin–carboxymethyl cellulose–graphene oxide composite materials and its application for removal of basic fuchsin, *J. Iran. Chem. Soc.* 14 (2017) 1827-1837
- [S13] Y.-B. Song, X.-D. Song, C.-J. Cheng, Z.-G. Zhao, Poly(4-Styrenesulfonic Acid-co-Maleic Acid)-Sodium-Modified Magnetic Reduced Graphene Oxide for Enhanced Adsorption Performance Toward Cationic Dyes, *RSC Adv.* 5 (2015) 87030-87042.
- [S14] P. Tan, Y. Hu, Improved synthesis of graphene/ β -cyclodextrin composite for highly efficient dye adsorption and removal, *J. Mol. Liq.* 242 (2017) 181-189.
- [S15] X. Yang, Y. Li, Q. Du, J. Sun, L. Chen, S. Hu, Z. Wang, Y. Xia, L. Xia, Highly Effective Removal of Basic Fuchsin from Aqueous Solutions by Anionic Polyacrylamide/Graphene Oxide Aerogels. *J. Colloid Interface Sci.* 453 (2015) 107-114.
- [S16] J. Fan, Z. Shi, M. Lian, H. Li, J. Yin Mechanically strong graphene oxide/sodium alginate/polyacrylamide nanocomposite hydrogel with improved dye adsorption capacity *J. Mater. Chem. A*, 1 (2013) 7433-7443

- [S17] H. Guo, Y. Wang, Y. Huang, F. Huang, S. Li, Y. Shen, M. Zhu, A. Xie, A GO@PLA@HA Composite Microcapsule: Its Preparation and Multistage and Controlled Drug Release, *Eur. J. Inorg. Chem.* 27 (2017) 3312–3321.
- [S18] Y. Ying, P. He, G. Ding, X. Peng, Ultrafast adsorption and selective desorption of aqueous aromatic dyes by graphene sheets modified by graphene quantum dots, *Nanotechnology* 27 (2016) 245703.
- [S19] S. Yang, L. Chen, L. Mu, P.-C. Ma, Magnetic graphene foam for efficient adsorption of oil and organic solvents *J. Colloid Interface Sci.* 430 (2014) 337-344.
- [S20] R. Wu, B. Yu, X. Liu, H. Li, W. Wang, L. Chen, Y. Bai, Z. Ming, S.-T. Yang, One-pot hydrothermal preparation of graphene sponge for the removal of oils and organic solvents *Appl. Surf. Sci.* 362 (2016) 56-62.
- [S21] S. Kabiri, D. N. H. Tran, T. Altalhi, D. Losic, Outstanding adsorption performance of graphene–carbon nanotube aerogels for continuous oil removal, *Carbon* 80 (2014) 523-533
- [S22] Z. Niu, J. Chen, H. H. Hng, J. Ma, X. Chen, A Leavening Strategy to Prepare Reduced Graphene Oxide Foams, *Adv. Mater.* 24 (2012) 4144-4150.
- [S23] H. Ren, X. Shi, J. Zhu, Y. Zhang, Y. Bi, L. Zhang, Facile synthesis of N-doped graphene aerogel and its application for organic solvent adsorption, *J. Mater. Sci.* 51 (2016) 6419-6427.
- [S24] J. Zhao, W. Ren, H.-M. Cheng, Graphene sponge for efficient and repeatable adsorption and desorption of water contaminations *J. Mater. Chem.* 22 (2012) 20197-20202.
- [S25] Q. Wu, Y. X. Xu, Z. Y. Yao, A. R. Liu, G. Q. Shi, Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films, *ACS Nano*, 4 (2010) 1963–1970.
- [S26] Y. Wang, J. Chen, J. Cao, Y. Liu, Y. Zhou, J.-H. Ouyang, D. Jia, Graphene/Carbon Black Hybrid Film for Flexible and High Rate Performance Supercapacitor, *J. Power Sources* 271 (2014) 269–277.

- [S27] J.-Y. Kim, K.-H. Kim, S.-B. Yoon, H.-K. Kim, S.-H. Park, K.-B. Kim, In situ chemical synthesis of ruthenium oxide/reduced graphene oxide nanocomposites for electrochemical capacitor applications, *Nanoscale*, 5 (2013) 6804–6811.
- [S28] Z. F. Li, H. Zhang, Q. Liu, L. Sun, L. Stanciu, J. Xie, Fabrication of High-Surface-Area Graphene/Polyaniline Nanocomposites and Their Application in Supercapacitors, *ACS Appl. Mater. Interfaces*, 5 (2013) 2685–2691.
- [S29] J. Yan, Y. Ding, C. Hu, H. Cheng, N. Chen, Z. Feng, Z. Zhang, L. Qu, Preparation of multifunctional microchannel-network graphene foams, *J. Mater. Chem. A*, 2 (2014) 16786-16792.
- [S30] D. Mhamane, S. M. Unni, A. Suryawanshi, O. Game, C. Rode, B. Hannoyer, S. Kurungot and S. Ogale, Trigol based reduction of graphite oxide to graphene with enhanced charge storage activity, *J. Mater. Chem.* 22 (2012) 11140–11145.
- [S31] Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang, X. Duan, Flexible Solid-State Supercapacitors Based on Three-Dimensional Graphene Hydrogel Films. *ACS Nano* 7 (2013) 4042–4049.
- [S32] Z. H. Wen, X. C. Wang, S. Mao, Z. Bo, H. Kim, S. M. Cui, G. H. Lu, X. L. Feng, J. H. Chen, Crumpled Nitrogen-Doped Graphene Nanosheets with Ultrahigh Pore Volume for High-Performance Supercapacitor, *Adv. Mater.* 24 (2012) 5610-5616.