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Electrolytic exfoliation of graphite in water with multifunctional electrolytes: en route towards high quality, oxide–free graphene flakes

J.M. Munuera, J.I. Paredes, S. Villar–Rodil,* M. Ayán–Varela, A. Martínez–Alonso,
J.M.D. Tascón

Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain

*Corresponding author: E-mail address: silvia@incar.csic.es (S. Villar–Rodil)

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S1. Experimental set–up

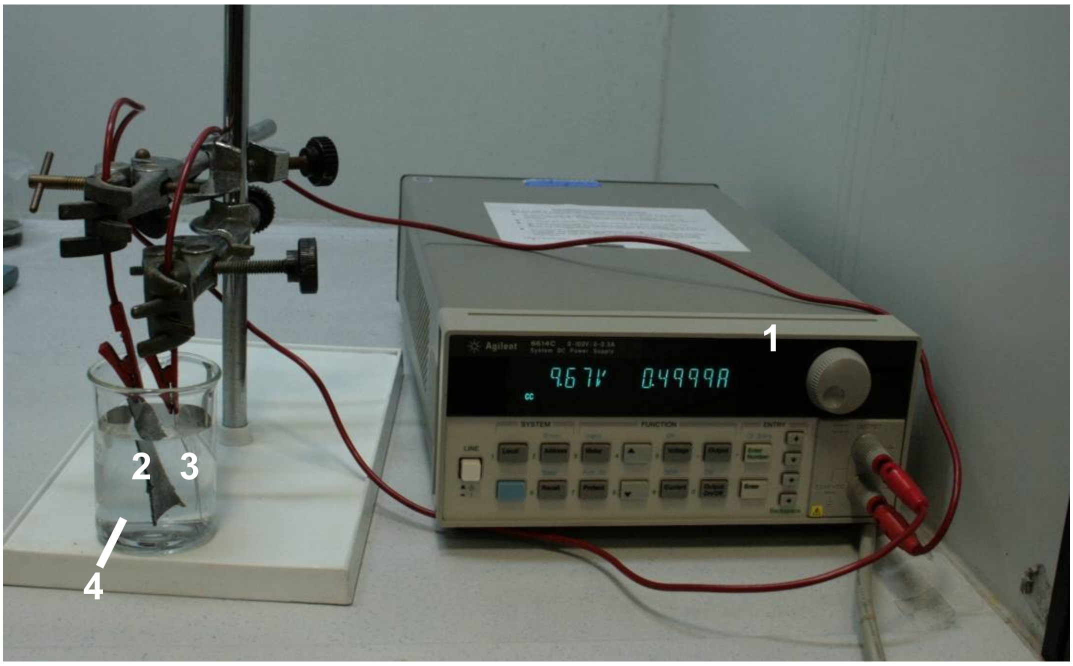

Figure S1. Digital photograph of the experimental set–up for the anodic exfoliation process consisting of an Agilent 6614C DC power supply (1) and two electrodes, namely, a graphite foil piece (40×25×0.5 mm^3) as working electrode (2), and a platinum wire as counter electrode (3). The platinum wire was placed parallel to the graphite foil surface at a distance of about 2 cm. The two electrodes were immersed in an aqueous solution (20 mL) of a given electrolyte at a certain concentration (4).

S2. Visual and microscopic evidence for the expansion of graphite foil upon anodic treatment

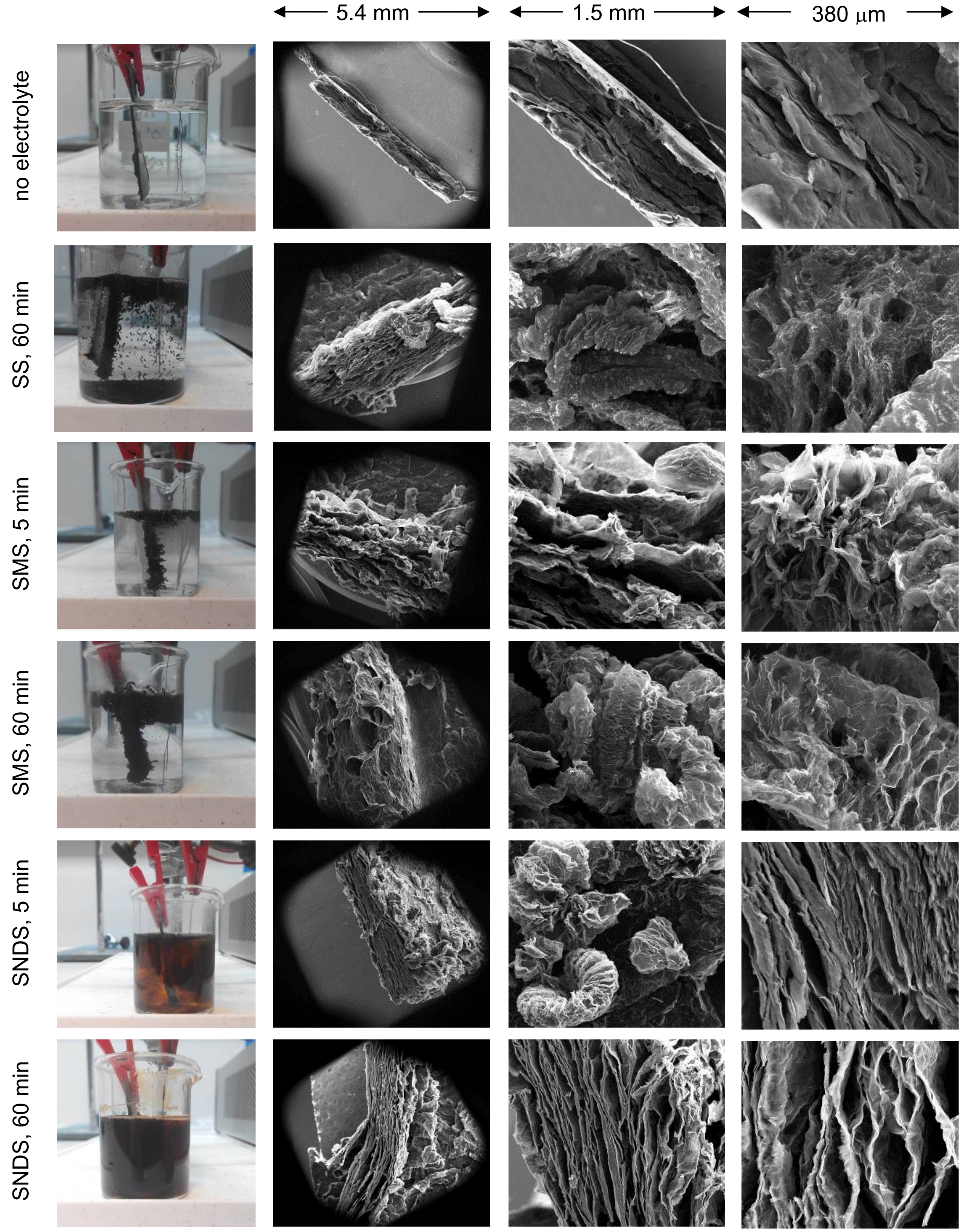

Figure S2. Digital photographs of graphite foil subjected to electrolytic treatment for the indicated periods of time in the presence of different electrolytes, namely, sodium sulfate (SS), sodium methanesulfonate (SMS), or disodium naphthalene–1,5–disulfonate (SNDS).

SEM images of the edge surface of graphite foil at increasing magnification for the different electrolytic treatments are also given.

Application of a positive potential of 10 V to a graphite working electrode in aqueous solutions of the specified electrolytes (see Fig. S1) led to the expansion and detachment of small fragments of material (up to a few millimeters), in line with recent studies on the anodic exfoliation of graphite in aqueous solutions of sulfate–based salts [1–2]. The vigorous expansion of the graphite slabs was noticeable even to the naked eye. The first column in Fig. S2 shows digital pictures of the beaker where the electrolytic process takes place in the presence of different electrolytes and for the treatment times indicated. On comparing any of the photographs corresponding to graphite subjected to electrolysis with that corresponding to the starting graphite foil in the absence of any electrolyte, the expansion of the foil becomes apparent. Further evidence for such an expansion could be gathered by examining the morphology of the edge planes of the graphite electrode by FE–SEM. The second, third and fourth columns in Fig. S2 gather representative FE–SEM edge plane views of graphite foil at increasing magnification following the indicated electrolytic treatment conditions. The edge plane surface of the starting graphite foil slab (first row in Fig. S2) exhibits a rather compact morphology. Anodic treatment in presence of any of the specified electrolytes brings about expanded structures, consisting of thin layers separated by large voids several micrometers wide. In some cases, the expansion takes place in a more or less homogeneous accordion–like fashion. In other cases, detached, worm–like structures of expanded graphite are observed.

S3. Evidence for the electrolytic treatment being the critical step in the exfoliation

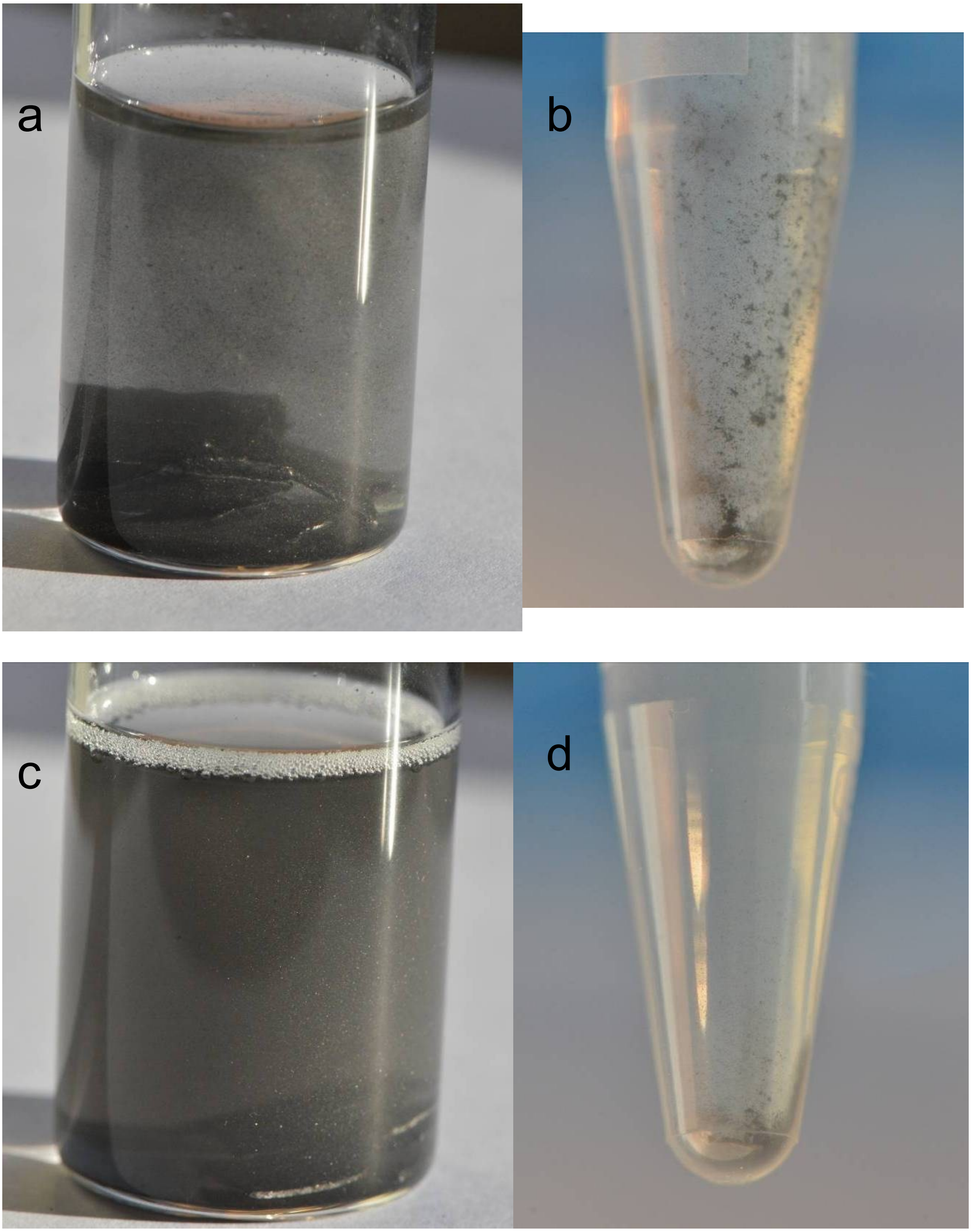

Fig. S3. Digital photograph of the dispersion of graphite foil obtained by ultrasonication for 3 h in the presence of 1 mg mL^{-1} SNDS before (a), and after centrifugation at 50*g* (b); in the presence of 0.1 mg mL^{-1} sodium cholate before (c), and after centrifugation at 50*g* for 20 min (d).

We have demonstrated in the main text that, through electrolytic treatment with a suitable electrolyte followed by ultrasonication, it is possible to obtain aqueous graphene dispersions from graphite foil, which are colloidally stable for weeks or months. In contrast, when the electrolytic treatment is omitted, and the graphite foil is only sonicated in the presence of the same electrolyte, colloidal dispersions cannot be prepared. For instance, the dispersions prepared in the presence of 1 mg mL^{-1} SNDS consist of quite large particles visible to the naked eye before centrifugation (Fig. S3a). A very mild centrifugation at 50*g* induces complete sedimentation of the particles (Fig. S3b), while the colloidally stable dispersions prepared with a previous electrolytic step withstand centrifugation at 200*g*. The same happens when a reportedly good dispersant for graphite, such as sodium cholate, is used (see Figs. S3c and d).

We interpret that ultrasonication detaches some graphitic fragments from the surface of the foil, but it does not exfoliate it significantly. Thus, the electrolytic step is essential for the effective exfoliation of the material into graphene. In conclusion, in the approach investigated here, the exfoliation process takes place mostly, if not exclusively, during the electrochemical treatment. As previously stated in the literature [3], ultrasonication is only needed to detach the pre–exfoliated material.

If HOPG is used as starting graphite material, ultrasonication alone does not lead to detached graphitic fragments in any significant amount (photographs not shown), as HOPG is a compact, very low surface area material. However, as we have demonstrated in a previous work [4], effective exfoliation of HOPG is possible though electrolytic treatment. Furthermore, we demonstrate below that colloidally stable graphene dispersions are obtained from HOPG though the same process as that described in the main text for graphite foil (see Fig. S13a and accompanying text).

Of course, as is well known, graphite powder can be effectively exfoliated by ultrasonication only. However, as we previously reported [4], the dispersed amount is higher if a previous electrolytic step is introduced (8–fold when SS is used as electrolyte). Therefore, even in the case of graphite powder, the electrolytic treatment is a major driver for the exfoliation process.

S4. AFM characterization of the samples

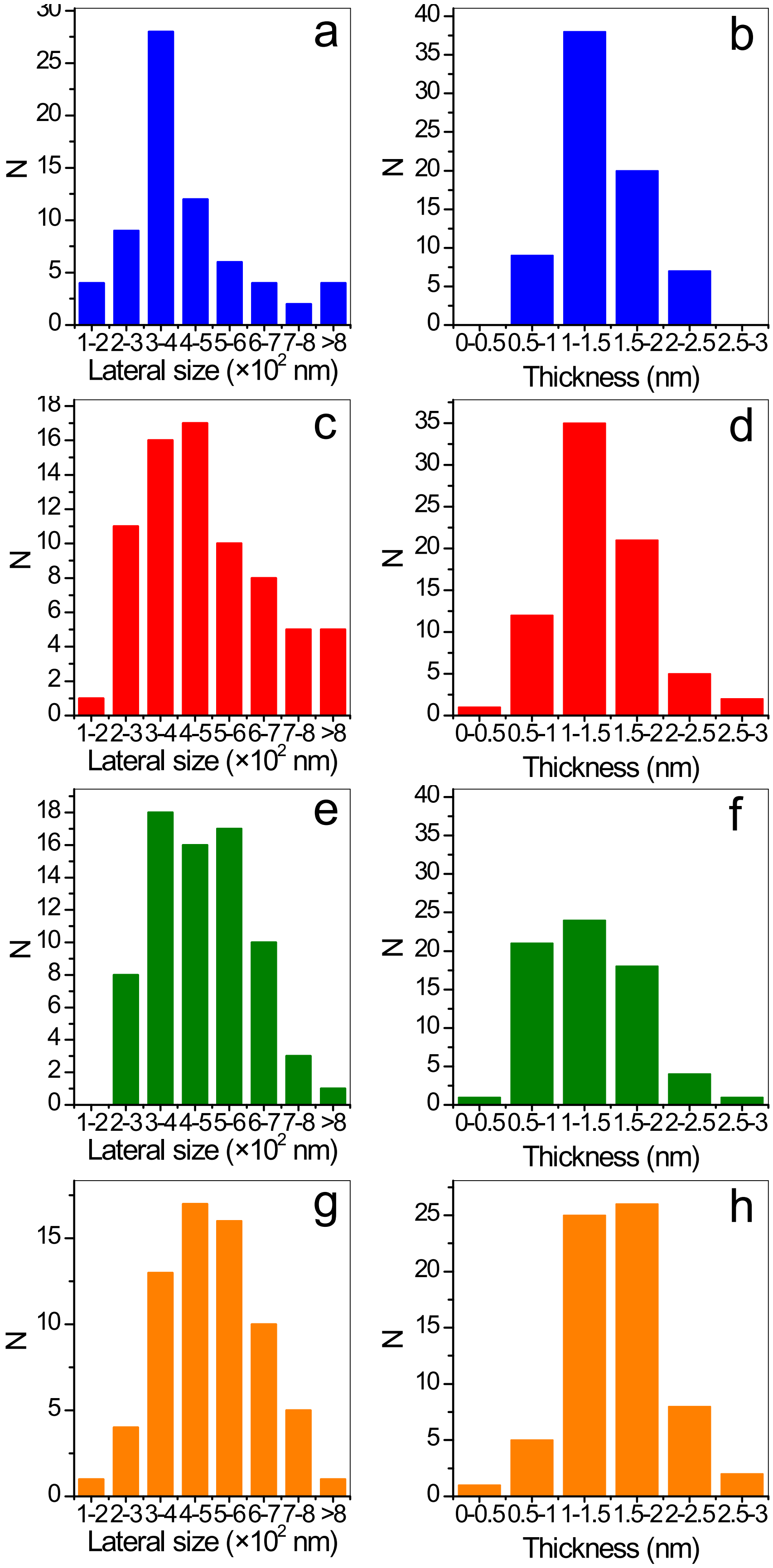

Figure S4. Histograms of flake lateral size (left) and apparent thickness (right) derived from a pool of 75 flakes measured from the AFM images of graphene dispersions obtained with 0.1M SS (blue columns), 0.05 M SBDS (red columns), 0.01 M SPTS (green columns), and 0.2M SNDS (orange columns).

The average apparent thickness for the graphene dispersions obtained with 0.1M SS, 0.05 M SBDS, 0.01 M SPTS, and 0.2M SNDS is 1.3±0.5 nm, 1.5±0.5 nm, 1.5±0.4 nm, 1.6±0.5 nm, respectively. Taking into account that the typical thickness of the patches of amphiphilic molecules adsorbed onto the HOPG surface (see Fig. 2d–f in the main text) was slightly above 1 nm and that these molecules are expected to contribute to the measured thickness of the flakes, we conclude the actual thickness of the flakes to be noticeably lower than that given in the histograms of apparent thickness of Fig. S4, and therefore consistent with the flakes being mostly single– to few(<5) –layer thick objects.

S5. XPS characterization of the samples

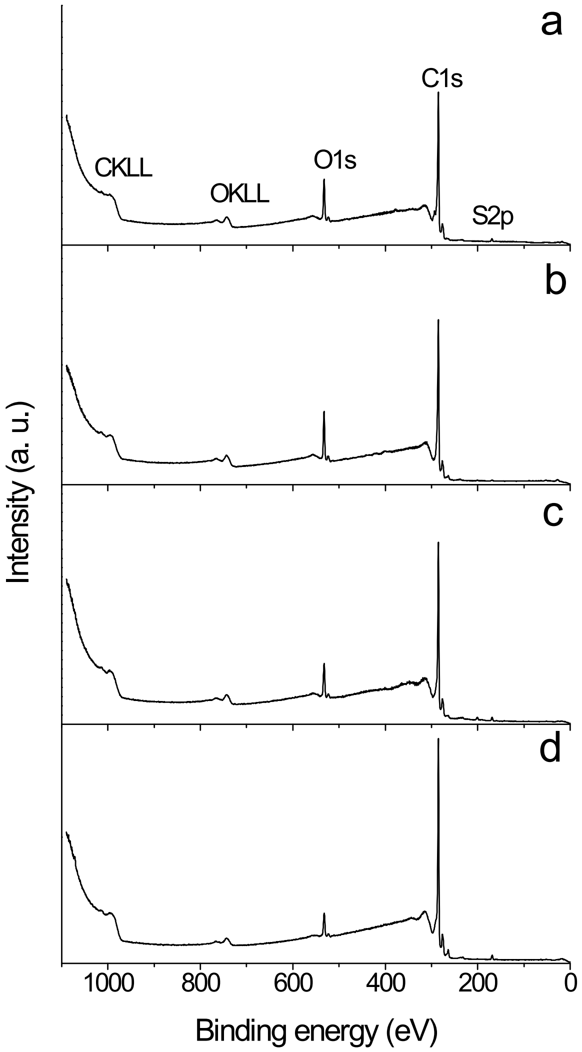

Figure S5. XPS survey spectra for graphene obtained with SS **(a)**, SBDS **(b)**, SPTS **(c)**, and SNDS **(d)**. The main XPS and Auger peaks have been labeled for clarity.

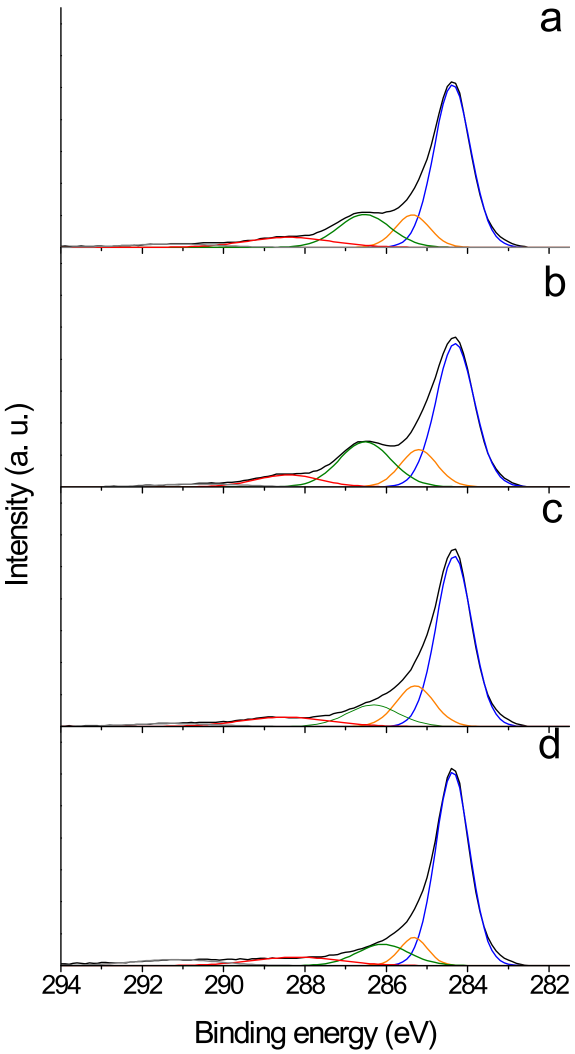

Figure S6. Background–subtracted, normalized, high resolution C 1s core level XPS spectra for graphene obtained with SS **(a)**, SBDS **(b)**, SPTS **(c)**, and SNDS **(d)**. The bands have been deconvoluted into 5 components, namely: graphitic carbon (blue trace); localized alternant hydrocarbon (orange trace); sp^3 carbon and C–O bonds in hydroxyl and epoxy groups (green trace); C=O bonds, carboxyls and $\pi \rightarrow \pi^*$ satellite band of the band at 285.5 eV (red trace); $\pi \rightarrow \pi^*$ satellite band associated to the graphitic carbon band (grey trace).

On deconvoluting the C 1s XPS band, it must be born in mind that the results can only be taken as semi–quantitative. In principle, deconvolution of the high resolution XPS C1s band could yield the type and relative amount of oxygen functionalities from the position of the maxima and the relative areas of the different components, which relate to different chemical environments of the C atom. This process is relatively straightforward for well–defined materials as polymers, where the known formula of a parent, non modified polymer can help with the identification of the different chemical functionalities and give an idea of the expected area ratios. In the case of relatively ill–defined carbon materials, apart from the lack of a suitable reference, there is the added problem of the metallic character of conducting, graphitic carbon, which is usually the principal component in the C1s envelope of any sp^2–based carbon material.

Herein, the C 1s band was allowed to fit to 6 symmetrical components with the following locations and assignments, [4,5]: at ~284.6 eV, graphitic structure whose electrons are extensively delocalized; at around 285.6 eV, defect sp^2 structure having electron delocalization less extensive than the former; at 286.6 eV, sp^3 hybridized free radicals but also C–O in hydroxyl and epoxy groups; at 287.8 eV, C=O bonds but also $\pi\rightarrow\pi^*$ satellite band of the band at 285.5 eV; at 288.9 eV, carboxylic groups; at ~291.5 eV, also $\pi\rightarrow\pi^*$ satellite band of the band at ~284.6 eV. Note the presence of multiple overlapping bands and the fact that the contribution of oxygen–containing functional groups to the total intensity will increase with the extent of oxidation while the intensity of the $\pi\rightarrow\pi^*$ satellite bands associated to conduction will simultaneously decrease in an unknown amount. When the bands were allowed to fit, just five bands were obtained: the bands for C=O and COOH are not resolved, yielding just one band at an intermediate location ~ 288.4 eV. It is noteworthy that the relative intensity of the component ascribed to hydroxyl and/or epoxy groups significantly diminishes when SPTS and SNDS are used as electrolytes, confirming their effectiveness in avoiding the oxidation of the graphene flakes.

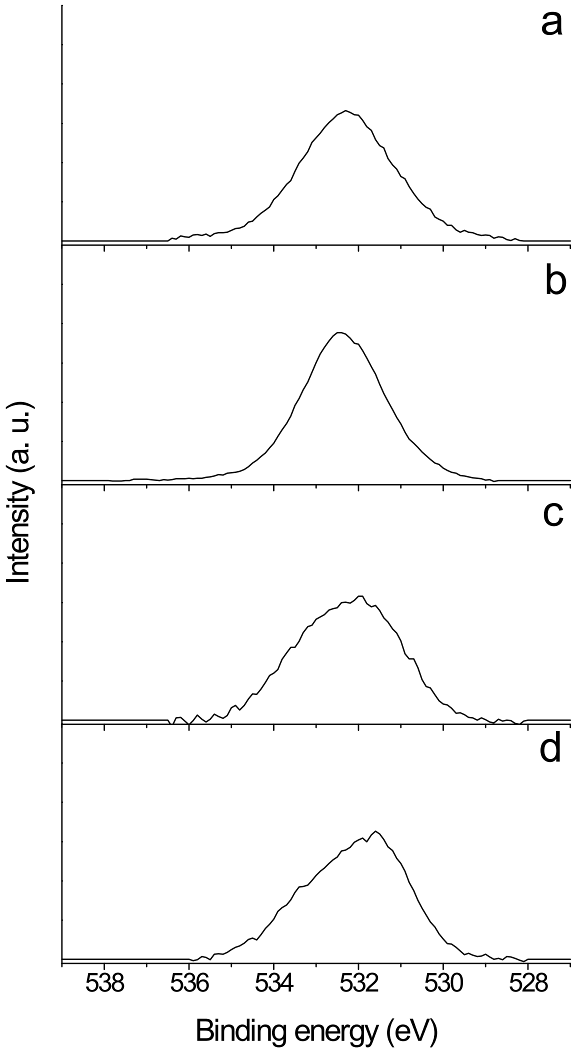

Figure S7. Background–subtracted, normalized high resolution O 1s core level XPS spectra for graphene obtained with SS **(a)**, SBDS **(b)**, SPTS **(c)**, and SNDS **(d)**.

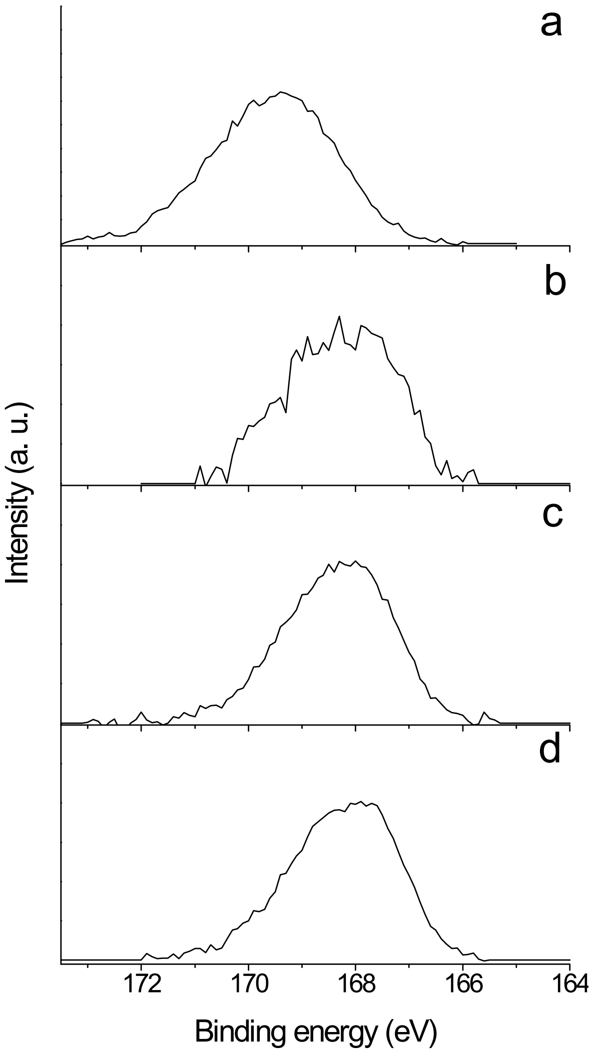

Figure S8. Background–subtracted, normalized high resolution S 2p core level XPS spectra for graphene obtained with SS **(a)**, SBDS **(b)**, SPTS **(c)**, and SNDS **(d)**.

Prior to XPS analysis, the samples were subjected to a special purification protocol to remove the largest possible fraction of amphiphile from the samples. However, a small amount remained. Indeed, some residual sulphur was detected in the samples (see survey spectra in Fig. S5). The high resolution S 2p spectra obtained after extensive accumulation indicate that, as expected, the sulphur present in the sample is of sulfate type in the case of graphene obtained with SS (Fig. S8a) and of sulfonate type for the rest of the samples (e. g., Fig. S8b–d).

S6. Measurement of film thickness by FE–SEM

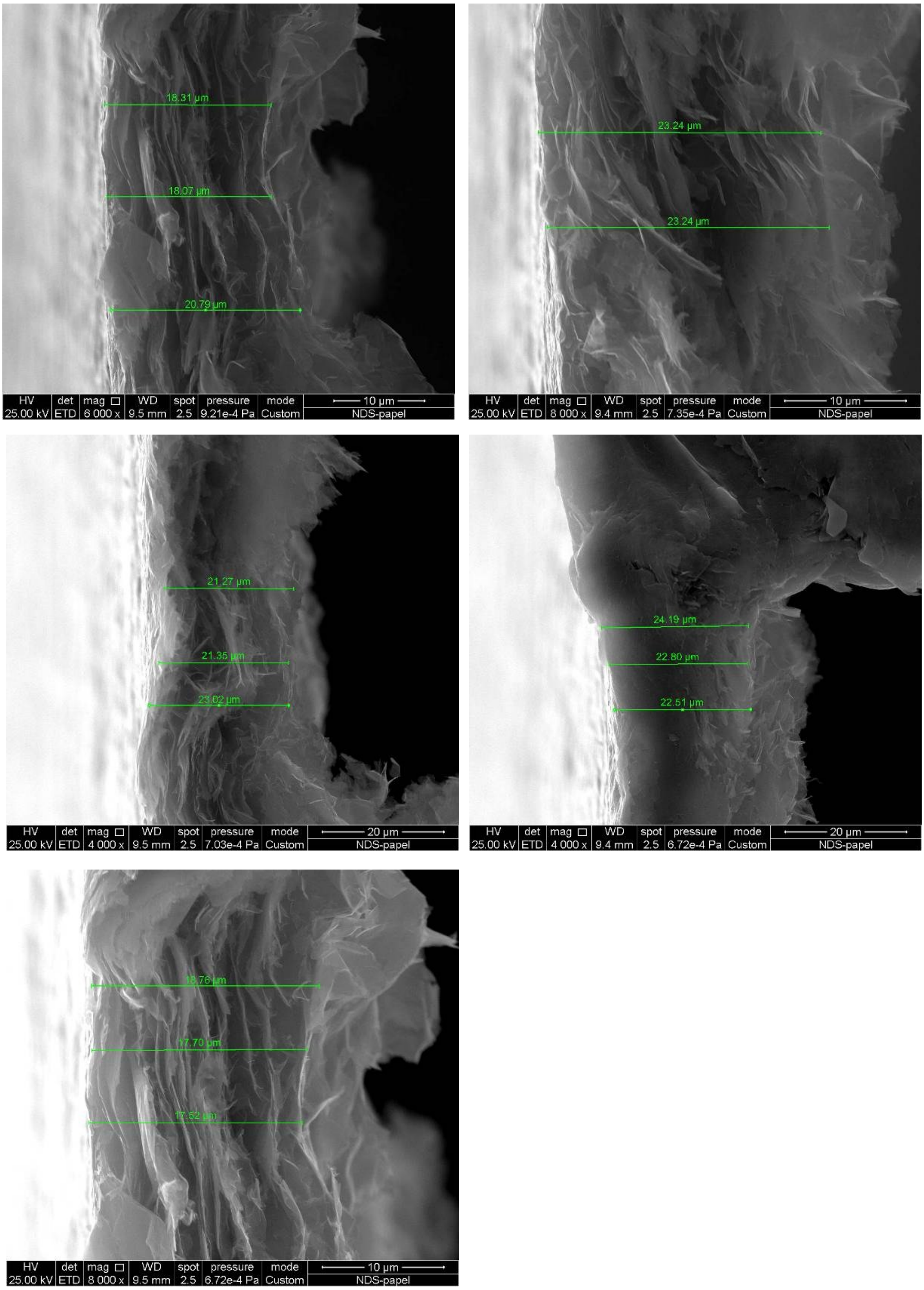

Fig. S9. FE–SEM images of the section of the graphene paper prepared with SNDS on which conductivity measurements were performed. The measurements of film thickness are indicated in green traces on each image. The average value obtained is 21±2 µm.

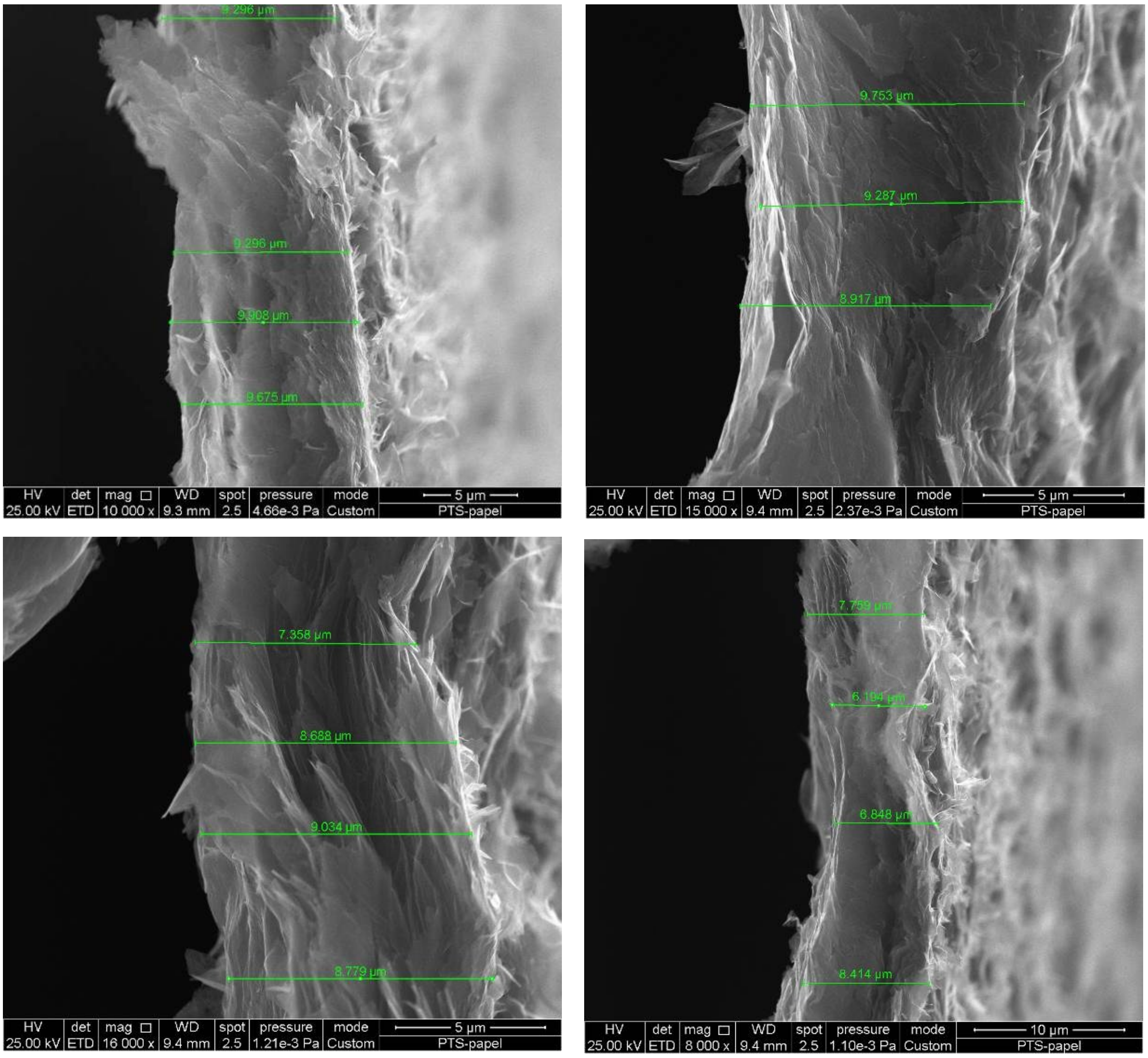

Fig. S10. FE–SEM images of the section of the graphene paper prepared with SPTS on which conductivity measurements were performed. The measurements of film thickness are indicated in green traces on each image. The average value obtained is 9±1 µm.

S7. Derivatization and XPS analysis of the graphene flakes obtained by anodic treatments using SS as electrolyte

A thin graphene film was prepared by drop–casting the graphene sample prepared by anodic exfoliation with SS as electrolyte and subsequently dispersed in water–isopropanol mixture on a pre–heated stainless steel plate. The sample was placed in a vial and introduced in a glove box with dry Ar atmosphere. After tempering for several hours, the sample was immersed in trifluoroacetic anhydride (Sigma–Aldrich) and the vial was closed to avoid the evaporation of the liquid. After 24 h, most of the liquid was removed and the rest was allowed to evaporate. The dry samples were transferred to the XPS equipment for analysis. Figure S11 shows the survey and the high resolution F 1s core level spectra for the treated sample.

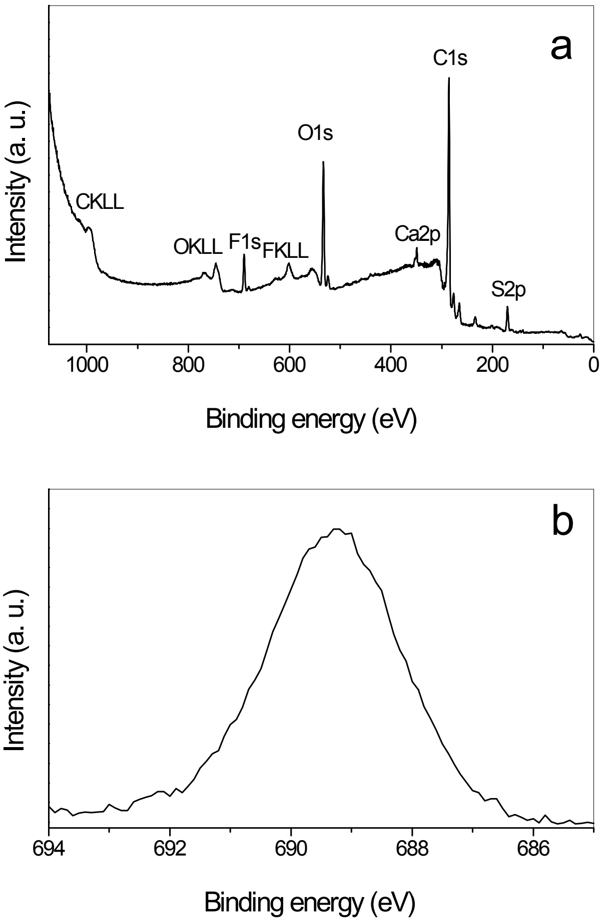

Fig. S11. Survey spectrum **(a)** and high resolution F 1s core level spectrum **(b)** for the graphene material obtained by electrolytic exfoliation with SS after derivatization with trifluoroacetic anhydride.

As seen in Fig. S11, F is incorporated to the sample after the treatment, which means that the derivatization reaction has taken place and confirms that there were indeed hydroxyl groups in graphene prepared with SS [6]. As a result of derivatization, each –OH group is expected to be substituted by O–CO–CF_3. Thus, if all the oxygen–containing groups in SS–exfoliated graphene were hydroxyls and they were completely derivatized, 3 F atoms would be incorporated to the structure for each oxygen atom originally present (and one additional O atom for every O atom originally present). Clearly, the amount of F incorporated (~3.5 at. %)

is less than thrice the original amount of oxygen in the structure (~11 at. %, see Table 1 in the main text). The additional O incorporated (~4 at. %) is also less than the original 11 at. %. However, this apparently low extent of derivatization comes partly from the fact that the reaction takes place strictly at the surface of the film, while XPS probes a few nanometers (~3 nm). Hence, the atomic composition yielded by XPS includes both the derivatized outer layers and the non–derivatized inner layers of the film. As the atomic composition is an average over the composition of both types of layers, this ~3.5 at. % of F incorporated to the material reflects a relatively high extent of derivatization and thus a relatively large amount of hydroxyl groups present in the original graphene.

S8. UHPLC/MS of the product of SNDS oxidation

In the main text, it has been argued that some electrolytes (most notably, SNDS) oxidize themselves during the anodic exfoliation process, which in turn prevents the oxidation of the exfoliated graphene layers. To show evidence of this, the electrolytic treatment of graphite foil using SNDS as electrolyte was carried out as described in the main text. Then, graphene was precipitated by ultracentrifugation at 20000*g* and the supernatant was subjected to 1:50 dilution in water and analyzed by ultra high performance liquid chromatography/ mass spectrometry (UHPLC/MS). The equipment was a UHPLC Dionex Ultimate 3000 RS liquid chromatograph (Thermo Scientific) equipped with a Bruker Impact II Q-ToF quadrupole–time of flight mass spectrometer (Bruker Daltonics GmbH). The obtained chromatogram is shown in Fig. S12.

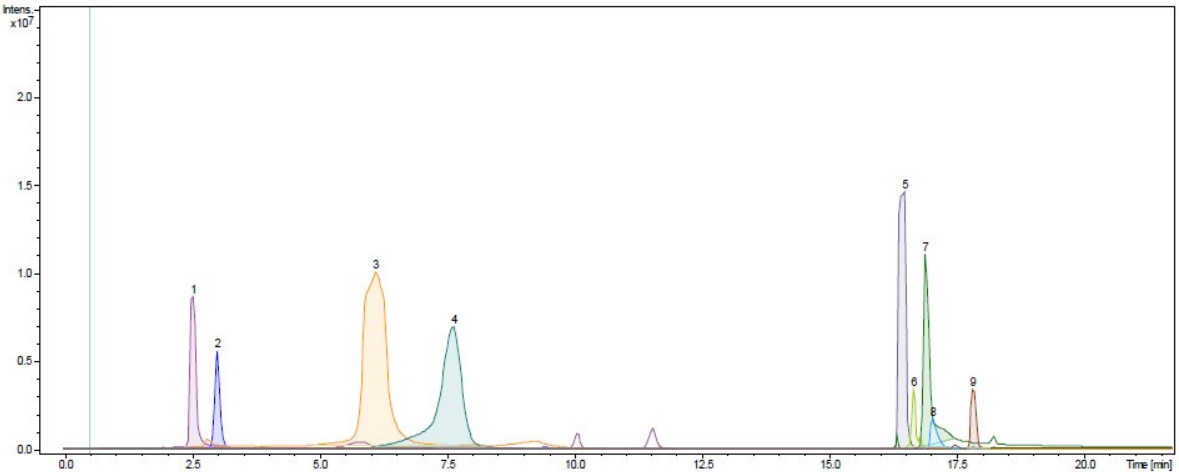

Fig. S12. Chromatograph for the supernatant obtained by precipitation of the graphene dispersion prepared by electrolytic treatment of graphite foil with SNDS.

The chemical formulas determined by MS and the corresponding average, nominal oxidation state for the C atoms of the separated products are the following:

1. $C_{10}H_8O_6S$: -0.2
2. $C_8H_6O_5S$: -0.25
3. $C_{10}H_6O_5S$: -0.2
4. $C_8H_6O_6S$: 0
5. SNDS: -0.6
6. $C_{10}H_{10}O_9S_2$: -0.4
7. $C_{10}H_7O_8S_2$: -0.3
8. undetermined mixture
9. mixture of $C_{10}H_7O_{10}S_2$ (+0.1), $C_{10}H_8O_{10}S_2$ (0), and $C_9H_7O_8S_2$ (-0.33).

Thus, oxidation of SNDS during the electrolytic exfoliation process is confirmed by the fact that the average, nominal oxidation state of the C atoms in every detected product is higher than that of the starting electrolyte.

S9. Demonstration for starting graphites other than graphite foil

The same protocol established in the main text for graphite foil was assayed for HOPG (grade ZYH, obtained from Advanced Ceramics) and natural graphite powder (grade 2910, from Mersen). For the electrochemical exfoliation experiments, ~10×10×2 mm^3 pieces of HOPG were employed, whereas the graphite powder was pressed into a circular pellet (12 mm in diameter, 2 mm in thickness) by means of a hydraulic press. These two additional graphite types have been treated in exactly the same conditions described in the main text for the electrolytic exfoliation of graphite foil in presence of 0.2 M SNDS, with the exception that in the case of natural graphite powder the electrolysis time was 3 min instead of 60 min. This short time is due to the quick detachment of the individual graphite particles from their pellet once they start to expand due to intercalation. Indeed, the individual graphite particles in the pelletized working electrode expand very quickly during the electrolytic process due to their small particle size, so that a graphite powder working electrode with a mass comparable to that of the HOPG electrode used here (or that of the graphite foil electrode described in the main text) was completely detached in 3 min.

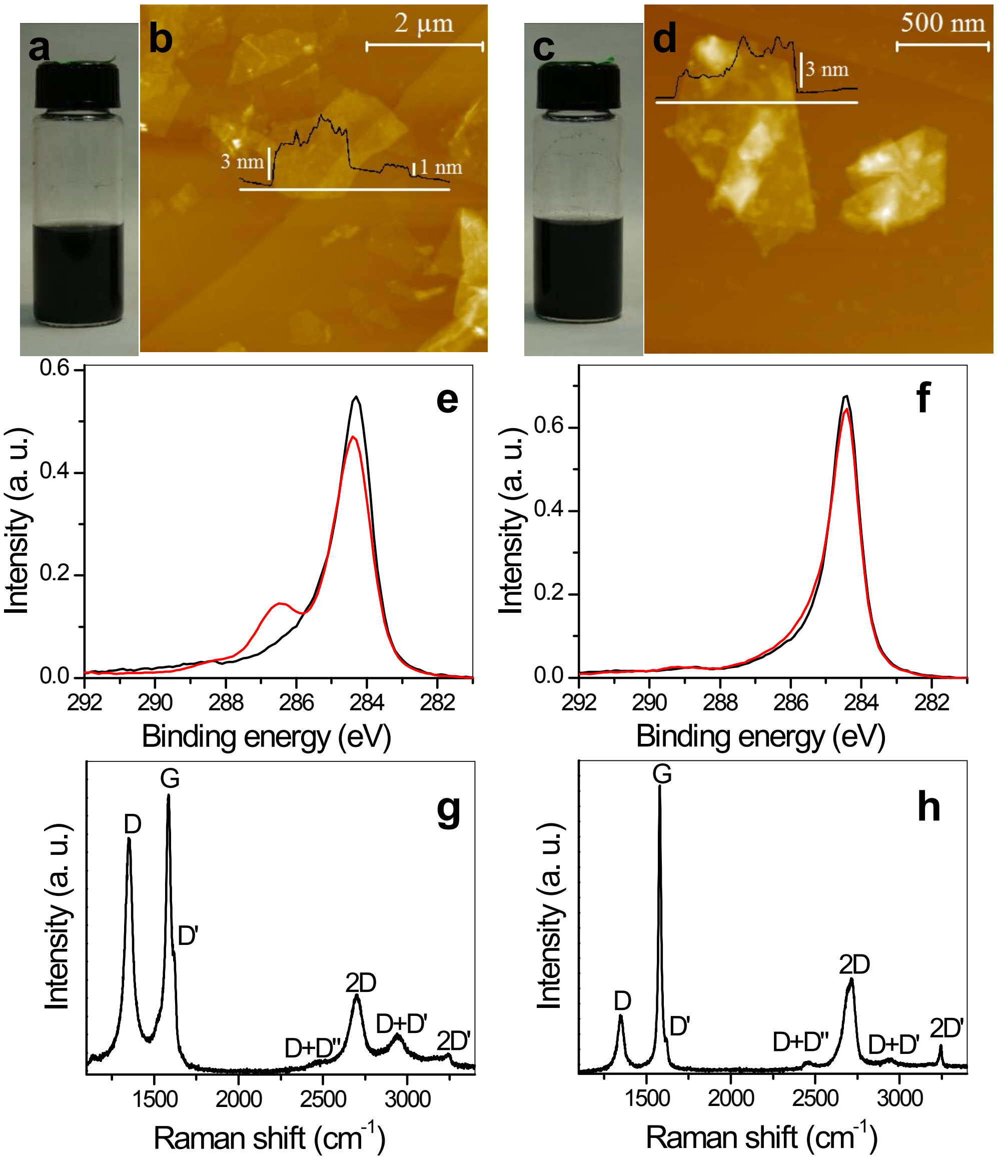

Figure S13. Digital photographs of the dispersions of HOPG **(a)** and natural graphite powder **(c)** prepared by electrolytic treatment at 10 V in 0.2 M SNDS aqueous solution followed by ultrasonication for 3 h. AFM images of the dispersions prepared from HOPG **(b)** and natural graphite powder **(d)** drop–cast onto HOPG substrates. A typical line profile (black trace) taken along the marked white line is shown superimposed on each image. Background–subtracted, normalized, high resolution C 1s core level XPS spectra of the drop–cast dispersions prepared from HOPG **(e)**, and natural graphite powder **(f)** with SNDS. For the sake of comparison, the C 1s spectrum of the drop–cast dispersions obtained with SS are also shown (red trace). Raman spectra of the flakes obtained from HOPG **(g)**, and natural graphite powder **(h)**. The main peaks are labeled.

Table S1. Characteristics of anodically exfoliated graphenes obtained from different types of graphite using sodium sulfate (SS) and sodium naphthalene 1,5–disulfonate (SNDS). The anodic exfoliation time is given in parenthesis.

graphite type	electrolyte	[electrolyte] (M)	[graphene] (mg mL^{-1})	Apparent thickness (nm)	O/C	I_D/I_G
Natural graphite powder	SS	0.10		3–4	0.04	0.2
(3 min)	SNDS	0.20	0.22	3–4	0.04	0.2
Graphite foil (60 min)	SS	0.10	0.66	1–2	0.11	1.0
	SNDS	0.20	0.84	1–2	0.02	0.2
HOPG (60 min)	SS	0.10		1–2	0.18	1.2
	SNDS	0.20	0.07	1–2	0.06	0.9

Electrolytic treatment led to homogeneous, opaque black suspensions (see digital photographs of the dispersions in Figs. S13a and S13c), which were colloidally stable for weeks. The effective exfoliation of the starting graphites into thin flakes was evident from the AFM images of the dispersions drop–cast onto HOPG substrates (Figs. S13b and S13d). The flakes showed typical lateral dimensions between a few and several hundred nm, and their apparent thickness, determined as flake height relative to the substrate (see exemplary line profiles in Figs. S13b and S13d), ranged between ~1 and 2 nm for graphene derived from HOPG (although a low proportion of flakes ~3 nm thick were found, see line profile in Fig. S13b), and between ~3 and 4 nm for graphene derived from natural graphite powder. As already found in a previous work [4], where the graphene dispersions obtained by anodic exfoliation of different types of graphite (using a common electrolyte, K_2SO_4) were compared, the exfoliation degree (flake thickness) tended to be better for graphene obtained from compact graphite types, such as HOPG or graphite foil, compared with graphene from particulate graphite types, such as natural graphite flakes and powder. This is due to the fact that the duration of the electrolytic exfoliation process is limited in the case of the particulate forms due to the quick detachment of the individual graphite particles from their pellets.

XPS analysis revealed that, in analogy with the results obtained for graphene from graphite foil, SNDS prevents to a significant extent the oxidation of graphene derived from HOPG compared with the use of a common electrolyte, such as SS. Indeed, the O/C ratios derived from XPS survey spectra are 0.06 for graphene obtained in the presence of SNDS vs. 0.18 for graphene obtained with SS (see Table 1).

The role of SNDS as a sacrificial agent to prevent graphene oxidation is also evident from the high resolution C 1s core level spectra (black and red trace in Fig. S13e for graphene obtained from HOPG using SNDS and SS, respectively). The significant drop in intensity of the component at ~286.5 eV assigned to carbon in hydroxyl and epoxy groups (C–O bonds) [6] is apparent when using SNDS. In the case of natural graphite powder, the degree of oxidation attained in the presence of common electrolytes, such as SS, is already low (O/C ratio of 0.04, see Table 1). Such low oxidation degree is due to the aforementioned limited duration of the electrolytic treatment (3 min). In this case, the oxidation degree remains unchanged if the electrolyte is changed to SNDS (see Table 1). This is also apparent from the high resolution C 1s core level spectra (Fig. S13f). However, in this case SNDS keeps the dual role of exfoliating electrolyte and colloidal dispersant.

Evidence of the structural quality of the anodically exfoliated graphene flakes was gathered by Raman spectroscopy. Representative Raman spectra of the drop–cast dispersions prepared from HOPG and natural graphite powder are presented in Figs. S13g and S13h, respectively. The corresponding integrated intensity ratio of the D and G bands (I_D/I_G ratio), which is indicative of the degree of structural quality in graphitic materials, is given in Table 1. Anodically exfoliated natural graphite powder using either SS or SNDS as electrolyte yield I_D/I_G ratio of 0.2 (vs. 0.1 for the starting graphite). As mentioned above, the short electrolytic treatment time limits the extent of oxidation of the flakes. Accordingly, the amount of defects and structural imperfections introduced in the carbon lattice are relatively small. In the case of HOPG, anodic exfoliation significantly increases the structural disorder, the I_D/I_G value increasing from 0 for the starting HOPG to 0.9 for the exfoliated flakes (See Table 1). However, the disorder introduced using SNDS as electrolyte is lower than when SS is used. Again, the presence of a sacrificial agent which diminishes oxidation brings about a lower number of defects.

Therefore, the results discussed in the main text for graphene obtained from graphite foil can be extended to other types of starting graphite. Indeed, with a suitable electrolyte it is possible to directly obtain colloidally stable aqueous graphene dispersions by anodic exfoliation of different types of graphite, with good exfoliation degree and reduced degree of oxidation. These results also confirm the conclusions of our previous work [4] where a comparison between graphene obtained from different starting graphites by electrolytic treatment with potassium sulfate was carried out. In that work it was concluded that graphene flakes with high structural quality and minimized amount of oxygen functional groups can be obtained by selecting appropriate types of graphite, such as graphite foil. A similar conclusion can be reached when using SNDS as electrolyte. This behavior was rationalized in our previous work in terms of the specific microstructure of the starting graphite material as well as the general exfoliation mechanism during the anodic process [4].

S10. Growth of Pt NPs on electrolytically exfoliated graphene in the absence of amphiphilic electrolyte

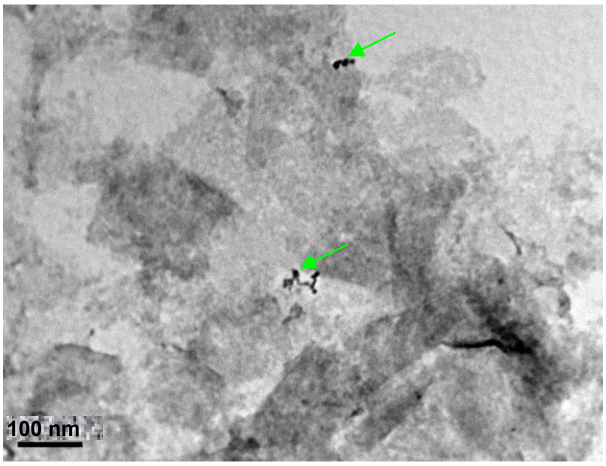

Figure S14. Representative TEM image of graphene–Pt NP hybrid obtained by the same protocol as that described in the main text for graphene–Pt NP hybrids but in the absence of any amphiphilic electrolyte. In this case, graphene was prepared by electrolytic exfoliation of graphite foil with the non–amphiphilic electrolyte SS and dispersion of the exfoliated product in a water–isopropanol mixture. Some NPs are marked by green arrows.

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