

Controlled Size Reduction of Liquid Exfoliated Graphene Micro-Sheets via Tip Sonication

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1 Article

2 Controlled size reduction of liquid exfoliated 3 graphene micro sheets *via* tip sonication

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16 **Abstract:** Liquid exfoliation of three-dimensional bulk solids having an inherent layered structure
17 is an effective and scalable method to produce stable to re-aggregation colloidal inks of 2D materials
18 suitable for solution processing. Shear-mixing is a relatively gentle technique that allows the
19 exfoliation by preserving the native lateral size of the 3D precursors, while tip sonication often leads
20 to extensive structural damage, producing 2D sheets where many edge defects are introduced. We
21 present here a mixed approach to obtain liquid dispersions of few-layers graphene flakes where the
22 average lateral size of the colloids can be tuned in a controlled way. The strategy relies on the
23 application of defined tip sonication steps on graphene inks prepared previously through the use
24 of a shear mixer, in this way starting from already exfoliated micro-sheets with limited amount of
25 edge defects. Our approach could represent a valuable method to prepare 2D materials inks with
26 **variable size distribution**, as differences in this parameter could have a significant impact on the
27 electronic behavior of the final material and thus on its field of application.

28 **Keywords:** few-layers graphene; liquid phase exfoliation; graphene ink; tip sonication; graphene
29 sheets
30

31 1. Introduction

32 The production of 2D materials through scalable methods that can preserve their quality and
33 ensure their industrial exploitation in a wide variety of devices^{1–4} and applications^{5–8} is a major
34 concern in nowadays applied research.⁹ Bottom-up approaches to produce them, such as epitaxial
35 growth on catalytic substrates through chemical vapor deposition¹⁰ or organic synthesis starting from
36 precursor molecules,¹¹ are not advantageous from an economical point of view for industrial-scale
37 production, unless highly pure single layer species are required. In order to find a cheaper and less
38 hazardous process for large scale graphene production, the liquid-phase exfoliation (LPE) methods
39 have been developed in the last few years.^{12,13} These techniques provide the system with the required
40 energy to overcome the van der Waals forces between layers in 3D crystals without increasing the in-
41 plane defects degree. The LPE process generally involves three steps, namely the dispersion of the
42 bulk material in a given solvent or water/surfactant solution, the exfoliation itself and the purification.
43 The last step (normally carried out through liquid cascade centrifugation) is necessary for the
44 separation of the exfoliated fraction from the un-exfoliated one and it affects the final concentration

45 of the 2D material ink. The choice of the solvent is also crucial as it determines the strength of the
46 solute-solvent interactions. The ideal solvent should minimize the interfacial tension between the
47 liquid and the 2D flakes in order to avoid the flakes to re-adhere to each other. In the case of LPE of
48 graphene, the best solvent identified to fulfill these requirements is undoubtedly N-cyclohexyl-2-
49 pyrrolidone (CHP), given the match in surface tension with that of graphite ($\gamma \sim 40 \text{ mJ m}^{-2}$).¹⁴

50 Among LPE methods it is convenient to distinguish between the use of shear-mixer type devices
51 and tip sonicators. The former feature an instrument head made of a rotor and stator: the rotation of
52 the inner part causes the formation of strong shear and thrust forces at which the mixture is subjected.
53 The procedure is controlled by hydrodynamic shear-forces under laminar flow in complete absence
54 of turbulence, avoiding the formation of in-plane defects. Paton et al. have shown that exfoliation
55 occurs whenever the local shear rate exceeds a critical value of around 10^4 s^{-1} .¹⁴ On the other hand, tip
56 sonication consists in a ultrasound-assisted exfoliation, during which hydrodynamic, shear-forces
57 associated with cavitation act on the bulk material and induce exfoliation. The exfoliation mechanism
58 is accompanied by fracturing processes, due to shockwaves generated by immediately adjacent
59 inertial cavitation activity, with the resulting effect of producing sheets with an elevated number of
60 edge defects.¹⁵

61 Here we report on the use of a two steps LPE method that allows the control of the average size
62 of few layer graphene sheets dispersed in CHP, with significant relevance for the future production
63 of size-defined graphene inks to be used for solution processing. This method consists in the previous
64 production of graphene micro sheets through shear-mixing starting from large-size graphite crystals
65 followed by the tunable reduction of the lateral sizes applying tip sonication protocols. We provide
66 a complete physico-chemical characterization of the thus produced size-controlled graphene inks that
67 allows the rationalization of the the effects of the sonication parameters employed on such a post-
68 synthetic method.

69 2. Materials and Methods

70 The EXG 3000 ink in CHP was prepared according to the procedure reported previously in ref
71 ¹⁶. Solvents were from Sigma-Aldrich and used as received. Shear-mixing LPE was carried out with
72 an IKA T25 digital shear mixer operating at 8000 rpm. The sample was cooled to 0 °C with an ice bath
73 during operation. Tip sonication was carried on a Baudelin Sonopuls tip sonicator operating at a 40%
74 and 60% power using pulses of 3s on/ 3s off. The samples were contained in 250 ml quartz beakers
75 kept in an ice bath. Raman spectroscopy was carried out using a Senterra Raman microscope working
76 with an excitation laser at $\lambda = 532 \text{ nm}$. All the samples were prepared by two consecutive
77 centrifugation steps of a mixture made with some drops of graphene suspension in EtOH to get rid
78 of the non-volatile solvent. The graphene/EtOH suspension was deposited on pre-cleaned oxidized
79 Si wafer and the solvent was evaporated. The focus was obtained with a 50x lens. The instrumental
80 settings were optimized and used for all the measurements: 5 sec, 40 co-additions, 5 mW of laser
81 power. DLS measurements were conducted with Malvern Zetasizer Nano-ZS device. The DLS system
82 was operated by the software Zetasizer from Malvern Panlytical. Instrumental settings adopted were
83 the following: 20 °C, toluene as solvent with a refractive index of 1.496 and graphene refractive index
84 2.411. The samples were prepared dissolving a drop of graphene mixture in toluene. The samples
85 were measured in Rotilabo® precision glass cuvettes with a light path of 10 mm and a volume of 3.5
86 mL. TEM images were acquired on a FEI Tecnai G2 microscope operating at 100 kV. HR-TEM and
87 SAED patterns were captured from samples created by drop casting lacy carbon grids with a FEI
88 Tecnai G2 20 X Twin instrument using 200 kV accelerating voltage. TGA was run **in air** on ~1 mg
89 sample using a Q5000 IR model TA instrument with the method of starting at 100 °C and kept
90 isothermal for 20 min, then ramping to 10 °C min⁻¹ up to 1000 °C. **UV-Visible absorption spectra were**
91 **acquired on a Goebel Uvikon spectrophotometer on original suspension in CHP further diluted with**
92 **dimethylformamide to achieve optical densities around 0.5.**

93 3. Results and Discussion

94 Some of us reported in a previous work¹⁶ the production of LPE graphene micro sheets of lateral
 95 sizes up to 50 μm or more and average number of layers around 5 starting from high-quality
 96 Madagascar graphite, employing the shear mixing method introduced by Paton et al. in CHP.¹⁴ The
 97 resulting ink is a stable to re-aggregation colloidal suspension, characterized by a concentration of
 98 graphene sheets in the range of 250-300 $\mu\text{g ml}^{-1}$.¹⁶ This colloidal sample is named EXG 3000 after the
 99 purification protocol employed. This consists in three subsequent centrifugation steps at increasing
 100 centrifugation speed, the last one being indeed carried out at 3000 rpm (1170 \times g) and allowing the
 101 isolation of the most exfoliated fraction within the mixture that underwent LPE. To this graphene
 102 micro sheets ink, tip sonication processes of different duration and power have been applied and the
 103 resulting products have been characterized by Raman spectroscopy, dynamic light scattering (DLS),
 104 transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) to provide a detailed
 105 picture in terms of average flakes sizes and defects distribution.

106 More in detail, three different ultrasonication treatments were applied starting from EXG 3000,
 107 which are summarized in Table 1 in terms of sonication power and time.

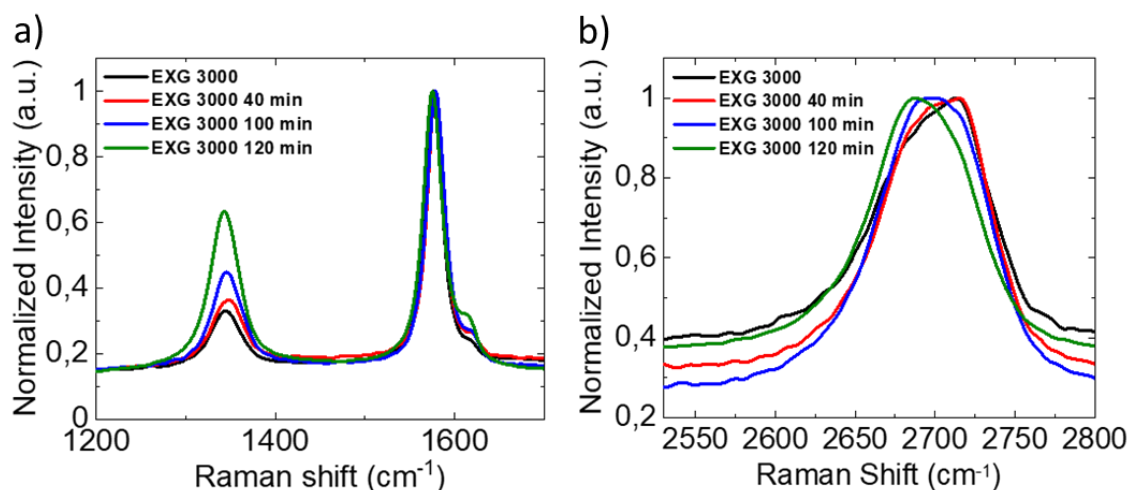
108 **Table 1.** Conditions applied for the ultrasonication of the graphene ink EXG 3000.

Sample name	Starting graphitic suspension	Nominal electrical input power (%)	Sonication time (min)
EXG 3000 40 min	EXG 3000	40 %	2 \times 20 ¹
EXG 3000 100 min	EXG 3000 40 min	40 %	2 \times 30 ¹
EXG 3000 120 min	EXG 3000	60 %	2 \times 60 ¹

109 ¹Between the two intervals a pause of 5 min was applied

110 As it can be inferred from this table, the protocol employed aims at verifying whether two
 111 subsequent sonication steps at short times and medium power (the first two entries in the table)
 112 differs from the application of one single long step at high power (last entry). The first-time interval
 113 of the two-step case was kept lower than 1 h to verify the effect of a relatively short initial sonication.

114 The products were first analyzed via Raman spectroscopy (Figure 1). In Figure 1a a section of
 115 the Raman spectra of the different samples is reported and, precisely, in the range in which the D
 116 (defects-related) and G (sp^2 structure-related) bands are located. The small shoulder appearing on the
 117 high wavenumber side of the G band is the so-called D' band.^{17,18} The intensity ratio between the D
 118 band (I_D) over the G band (I_G) was evaluated for the three samples and for EXG 3000 and the resulting
 119 values are summarized in Table 2.



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Figure 1. Raman spectroscopy analysis on the ultrasonicated EXG 3000 samples and on pristine EXG 3000. a) Detail of the D and G bands with relative intensity normalized on the G peak. b) Detail of the 2D band.

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Table 2. Relevant intensity ratios between Raman peaks in Figure 1a.

Sample name	Average I_D/I_G^1	Average I_D/I_D^1
EXG 3000	0.382 ± 0.030	1.15 ± 0.02
EXG 3000 40 min	0.390 ± 0.025	0.97 ± 0.02
EXG 3000 100 min	0.431 ± 0.021	1.75 ± 0.01
EXG 3000 120 min	0.667 ± 0.058	1.47 ± 0.04

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¹ Average of five measurements in different points of the sample

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The D band intensity clearly increases with the time and power of sonication applied. This is particularly evident for the sample sonicated in one single step for a long time and with a high power (EXG 3000 120 min), while for the sample sonicated at the shorter time slot (EXG 3000 40 min) the increase is relatively low. The observed trend could be related to the presence of a greater number of defects either at the edges or in the basal plane. In the first case, a greater number of edges could be correlated to a decrease of graphene flakes lateral size, while in the second case defects located in the basal plane could be generated as a side-effect of the sonication energy applied. To distinguish between the two types of defects, the intensity of the D band (I_D) over the D' band ($I_{D'}$) was evaluated in order to verify the nature of defects (Table 2), according to Eckmann et al., that demonstrated how the value of the $I_D/I_{D'}$ ratio depends only on the types of defects rather than on their quantity.¹⁸ For each sample, the value of the $I_D/I_{D'}$ ratio evaluated is smaller than 3.5, a threshold that indicates the presence of edge defects. The other kind of defects on the crystal structure of graphene, i.e. sp^3 carbons and vacancy, are characterized by higher ratio values. Hence, the major effect of the sonication step was to reduce the graphene flakes size. The higher the sonication power, the smaller the flakes and consequently the more the edges.

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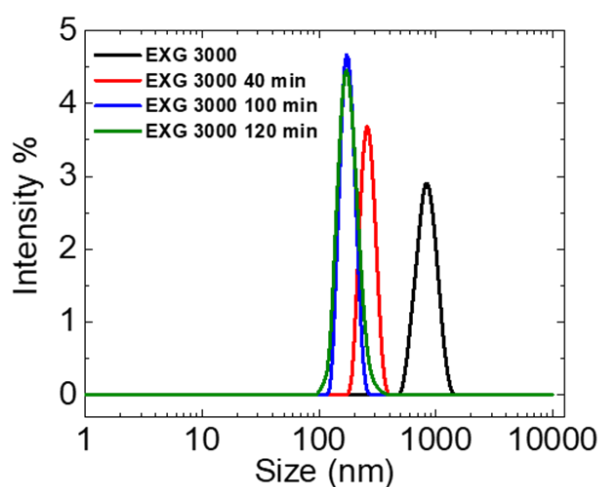
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The analysis of the 2D band (Figure 1b) shed light on other interesting information about the degree of exfoliation and how it is affected by the sonication step. Indeed, 2D band shape and shift of the maximum are heavily affected by the number of graphene layers present in an analysed sample.¹⁷ In single layer graphene, the intensity of the 2D (I_{2D}) peak should be roughly four times I_G and it should quickly decrease as the number of layers increases. In the here analysed samples, I_{2D} was found to be about half of I_G . Hence, in the inks few layers graphene predominates over single

147 layer. This result is also confirmed by the value of the full width at half maximum (FWHM) of the 2D
148 band. The FWHM is larger than 50 cm^{-1} and it almost doubles the one of the single layer graphene 2D
149 peak. Nonetheless, the corresponding peaks show a progressive down-shift of more than 25 cm^{-1} in
150 respect to the starting material (Figure 1b), accountable to a contemporary flake exfoliation during the
151 sonication step.¹⁹ Through the qualitative analysis of the 2D band shape, within which two
152 components can be distinguished at around 2725 and 2675 cm^{-1} that change in relative intensity in
153 relation to the number of layers in the specimen, as described in detail by Ferrari et al. in ref. ¹⁷, it is
154 clear that the layers number progressively decreases by increasing time and power of sonication, as
155 the intensity of the 2725 cm^{-1} component progressively decreases while the 2675 cm^{-1} one increases.
156 Moreover, the more sonicated samples show a similar 2D band shape and so it is their degree of
157 exfoliation. In particular, the sample to which one single long and high-power sonication step was
158 applied (EXG 3000 120 min) results to be the one in which the 2D band shape and position of the
159 maximum recalls more closely that of single layer graphene. Indeed, the rate of exfoliation of
160 graphene flakes becomes slower if their size decreases and as a consequence it is hard to further
161 exfoliate the smaller flakes in suspension.²⁰

162 The quantitative analysis of the flakes sizes was conducted via DLS. The technique could give
163 reliable results on colloidal sizes only for spherical particles, while graphene flakes are almost
164 completely planar. However, in this case DLS results were not used to define the hydrodynamic
165 diameter of the flakes but to search for a trend resulting from the controlled sonication processes.
166 Indeed, it is evident that smaller flakes can be obtained with longer and stronger ultrasonication step
167 (Figure 2). In particular, DLS analysis reveals that flakes size drastically decreases after 40 min of
168 sonication but there are just minor changes for further sonication times. In fact, the hydrodynamic
169 diameter obtained for the sample after the 120 min cycle sonication is similar to the one obtained after
170 the 100 min cycle in two consecutive steps of 40 and 60 min.



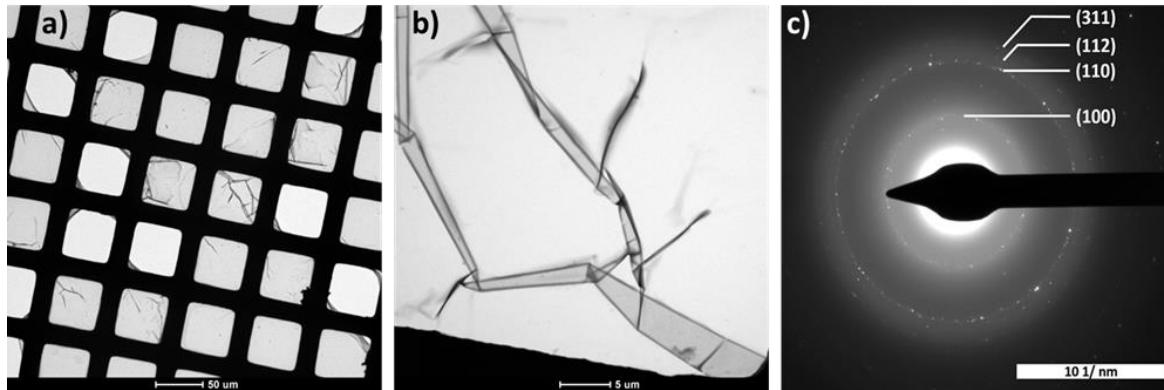
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Figure 2. DLS spectra of the ultrasonicated EXG 3000 samples and of pristine EXG 3000.

173 More detailed information on the sample morphologies are obtained by performing TEM and
174 high-resolution (HR-TEM) analysis. Figure 3 reports the TEM images at lower and higher resolution
175 of the starting LPE ink EXG 3000. The considerable lateral extension of the graphene sheets contained
176 within the colloidal suspension is well evident from the left image, where the flakes appear to be
177 covering a large part of the TEM grid. More in detail, from the right image it is possible to notice that
178 such a remarkable size extension (which originates by the fact that shear mixing is not a destructive
179 method to perform graphite exfoliation and the starting Madagascar graphite sample was constituted
180 of very big crystals¹⁶) causes the flakes to fold in some point, forming sort of wrinkles. Selected area
181 electron diffraction (SAED) in Figure 3c shows the presence of reflections typical of a graphite-like
182 sp^2 carbon phase (those indicated as 100, 110 and 112) and a very weak signal of a reflection
183 assignable to a diamond-like phase, and thus sp^3 carbon (the one indicated as 311), probably due to
184 the existing sp^3 defects in the sample that give rise to a non-zero D-band in Figure 1a (black line).¹²

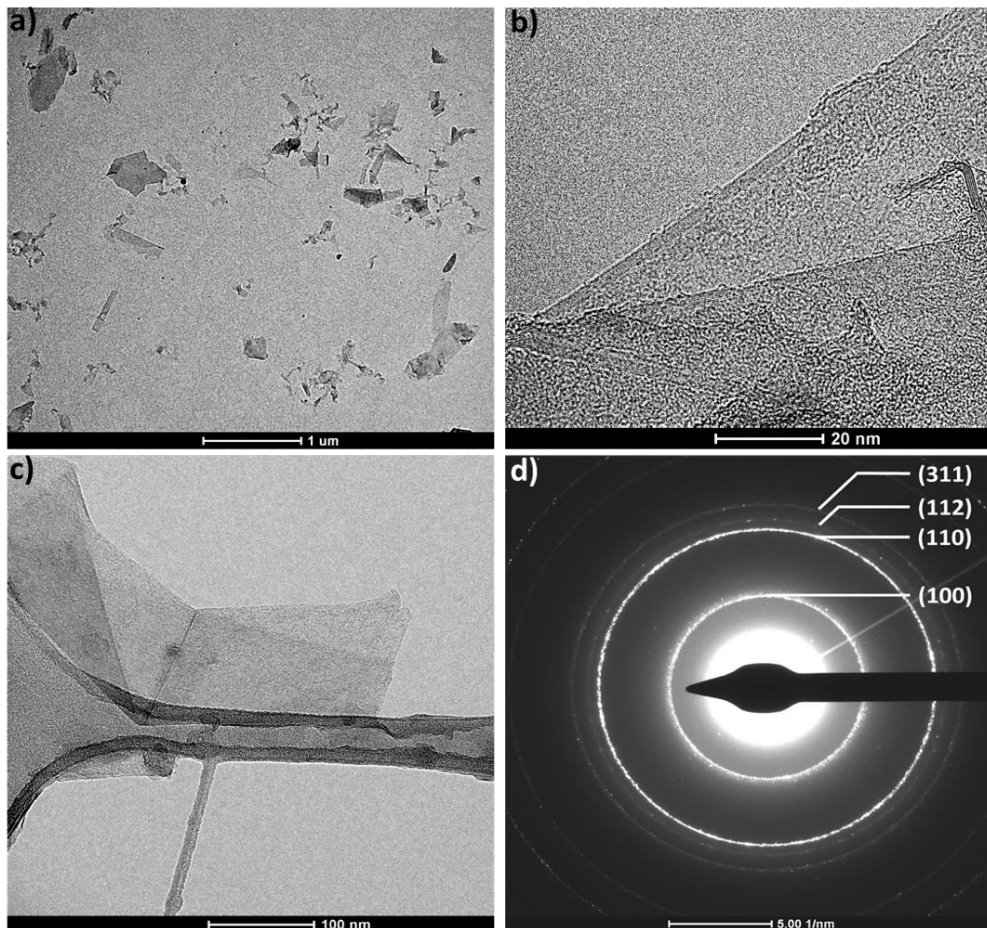
185 Given the lateral extension of the sample it is difficult to identify edges and therefore such a weak
 186 sp^3 carbon signal could be due to defects present in the basal plane of the flakes (which could have
 187 been present already in the pristine graphite).
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190 **Figure 3.** TEM images of EXG 3000 showing the considerable size of the graphene flakes present in
 191 the sample (left image at lower magnification) and their wrinkled nature (right image at higher
 192 magnification).

193 The sonication at 40 min of EXG 3000 at medium power (EXG 3000 40 min) causes a considerable
 194 reduction of the flake sizes that do not surpass the 1 μm threshold, with the smallest components also
 195 featuring lateral extensions of 50-100 nm (Figure 4a). HR-TEM allows to examine precisely the nature
 196 of the exfoliation, confirming what seen from Raman analysis of the 2D peak, i.e. a not considerable
 197 difference in number of stacked layers from the pristine EXG 3000 sample (around 5, Figure 4b).

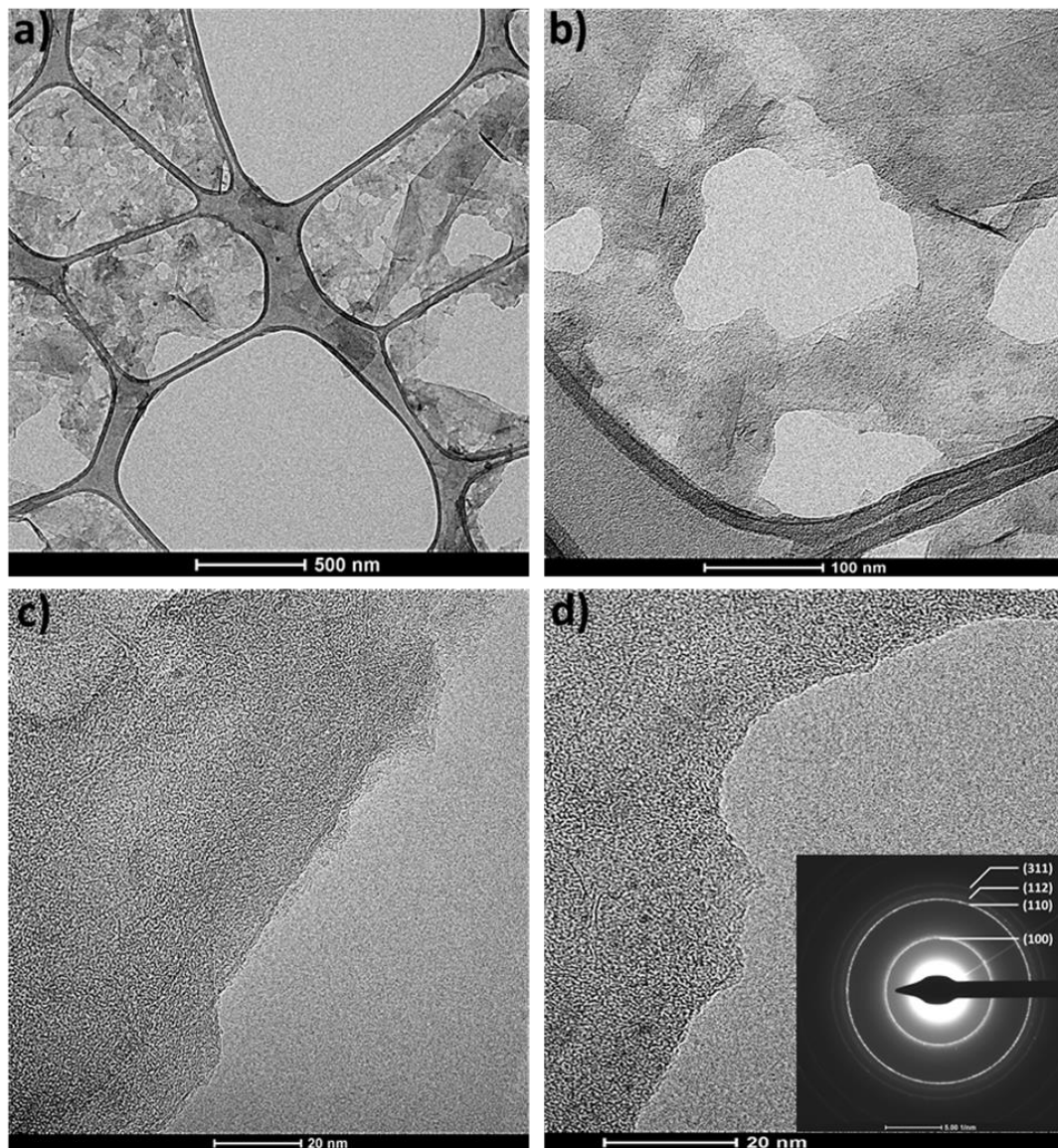


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199 **Figure 4.** Transmission electron microscopy characterization of the EXG 3000 40 min sample. a) Low
200 magnification TEM image of the sample. b) HR-TEM high magnification detail showing a number of
201 superimposed graphene layers in the samples equal to 5. c) HR-TEM detail on the geometrical shape
202 of the flake edges. d) SAED of the edges with indicated number of the identified reflections (see text
203 for speciation).

204 While the breaking of the flakes is extensive, the action of the sonication process on the 2D
205 material edges appears to be relatively regular, with the overall morphology in these parts
206 maintaining defined angles and straight lines, and with no sign of holes formation within the basal
207 planes. The nature of the defects at the edges is difficult to predict, nonetheless selected area electron
208 diffraction (SAED) could provide interesting hints on this aspect if addressed specifically onto this
209 part of the flakes. **Figure 4s shows the SAED patten obtained by selectively focusing on a flake edge,**
210 **from which the graphite-like reflections 100, 110 and 112 are still detected and the diamond-like**
211 **reflection 311 results considerably more visible than in the starting EXG 300 sample (Figure 3d).²¹**
212 **This increase in intensity** could be an indication that some of the defects created at the sheet edges
213 through prolonged sonication are carbon atoms in tetrahedral form. **On the other hand, their**
214 **distribution should give rise to areas with a crystalline order (also if very small ones), as otherwise**
215 **they could not give rise to a detectable diffraction pattern.**

216 The average size of the flakes that underwent the second step of sonication at low power (EXG
217 3000 100 min) and that of those coming from the single step high power treatment (EXG 3000 120
218 min) resulted to be very similar and extending in the range of few hundreds nm (between 100 and
219 500 nm maximum). The latter sample was further analyzed through HR-TEM, showing the formation
220 of peculiar morphologies at the edges, where irregular shapes are found as a result of the aggressive
221 treatment. Figure 5 reports a summary of these features: in the two top panels (Figure 5a and 5b) it is
222 possible to notice the formation of holes in the basal plane of the flakes having different
223 dimensionalities and an irregular geometry. These patterns are anyway to be considered as edges
224 and not as in plane defects, given their considerable extension. The increased level of exfoliation is
225 seen by focusing on edge areas where the highly irregular trend is not present, as the one highlighted
226 in Figure 5c. Number of superimposed graphene flakes between 2 and 3 are thus identified, while
227 monolayers are mainly found where the disordered damage is located, with an example in Figure 5d.
228 In these rugged edges the same sp^3 carbon SAED signature described above (Figure 4d) can be
229 detected, together with those typical of graphite (**inset of Figure 5d**).



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Figure 5. HR-TEM images of EXG 3000 120 min. The pronounced nature of the damage caused by prolonged sonication of the starting EXG 3000 sample is seen in these images with a), b) the generation of holes in the basal planes of the nano-sheets, c) a more extensive exfoliation and d) a rugged morphology at the edges.

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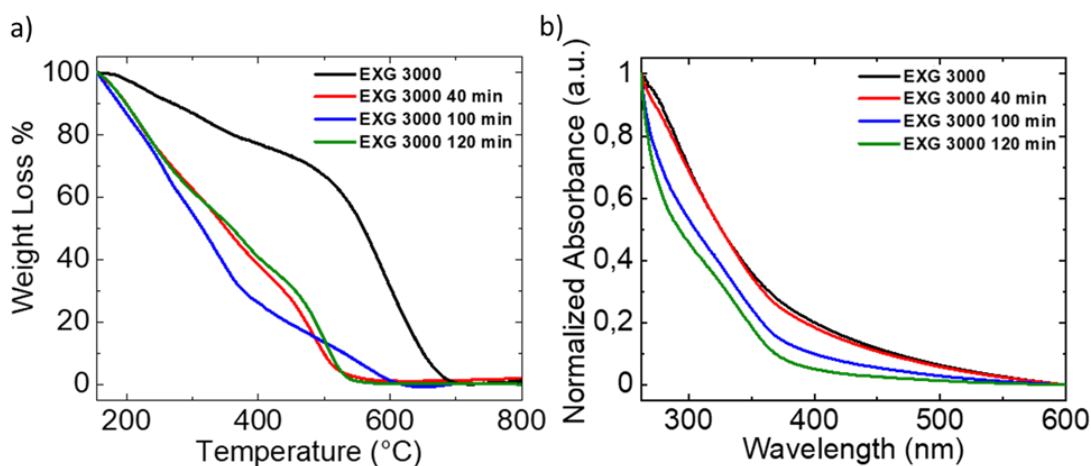
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The sonicated samples were further analyzed for their thermal behavior, by performing TGA in air to determine the decomposition temperature. Already for EXG 3000 a not net transition was identified (like the one of pure graphite), as the material was found to start with a little degradation already at around 250 °C. Nonetheless a decomposition temperature of 490 °C was extrapolated at the intersection of two linear fits encountering where the slope of the decomposition curve was most pronounced.¹⁶ The sonication treatment increases considerably this progressive weight loss as a result of increased temperature in the presence of oxygen, with an almost 80% of the initial mass of the specimen decomposed at 450°C and the remaining 20% completed within a 50 °C step ahead for the EXG 3000 sample sonicated for 40 min (red curve in Figure 6). The second step of sonication then further worsen the thermal stability (blue curve in Figure 6), with an initial drop of weight even more considerable. On the other hand, the sample sonicated in one single high power and long step features a thermal behavior similar to the EXG 3000 40 min one, indicating that the two materials could have similar stabilities, despite the different morphology and average sizes.



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Figure 6. a) Thermograms in air of the ultrasonicated EXG 3000 samples and of pristine EXG 3000.
b) UV-Visible absorption spectra of the ultrasonicated EXG 3000 samples and of pristine EXG 3000.

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We finally carried out an UV-Visible spectroscopic characterization of the ultrasonicated samples and compared their spectra with that of pristine EXG 3000, in order to verify the effect of extensive flakes damage on the optical and plasmonic properties of the dispersed graphene sheets. As it can be inferred from Figure 6b, a constant decrease in absorption along the whole visible range is detected for the two samples that underwent the longest sonication treatments (i.e. EXG 3000 100 and 120 min), while the sample sonicated for the shortest time (EXG 3000 40 min) maintains an absorption profile similar to that of the pristine material. Such a deterioration in the optical response resulting for the smallest produced nanosheets points out at a modification of the plasmonic response in the material, where likely electrons have lower freedom to move along a surface with a high amount of defects compared to the case of an extended micro sheet and thus start to feel a sort of confinement (which at the extreme cases would lead to the obtainment of graphene quantum dots, thus fully 0D materials).

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4. Conclusions

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We have reported here on a new approach to produce LPE graphene inks in CHP where the size and defects profiles of the suspended micro-sheets can be controlled by applying ultrasonication post-synthetic parameters. The size reduction of the starting micro-sheets was found to be considerable already at the shortest sonication time evaluated (40 min) leading to the formation of nano-sheets, suggesting that a very short or intermediate duration could provide lateral extensions that remain in the μm range. The effect of high power and time was seen to generate holes in the basal planes having variable sizes and geometries but still to be considered as edge defects given the relatively large extension, as the presence of real in plane defects should provide a different value for the I_D/I_G ration in the Raman spectra (these last type of defects are most likely individual sp^3 carbon moieties generated in a scattered manner on the sheets as an effect of, for example, a chemical treatment like functionalization¹⁸). In addition, an interesting perspective on the nature of the thus formed edge defects was provided through the use of SAED analysis, suggesting that ordered sp^3 carbon structures could be formed at these sites as an effect of sonication.

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Our data provide a valid platform for future studies aiming at determine the effect of different sizes and defects distribution on the properties of LPE graphene samples, with potential application also at other 2D materials inks. As a perspective for future work, a more thorough determination of the effect of shorter and less aggressive sonication procedures will be investigated, allowing to complete the scenario here presented, also through a better morphological characterization of the obtained species (for example through atomic force microscopy). In addition, a better understanding

284 of the modification induced in the electronic properties of the samples following the tip-sonication
285 treatment is necessary. The changes observed in the optical absorption profiles of the sonicated
286 materials compared to the pristine EXG 3000 sample provide first hints on existing variations in the
287 plasmonic (and consequently electronic) response,²² but other means have to be identified to better
288 describe them, such as electrochemistry, conductive atomic force microscopy or charge transport
289 measurements. The thus produced and characterized graphene inks could have a large interest for
290 multiple applications where the size of the flakes and their defects identity is relevant, going from
291 solution processed thin layers and devices to composites. They could even represent starting
292 materials for selective chemical functionalization strategies²³⁻²⁵ aiming at specific sites on the sheets^{26,27}
293 such as the edges or the holes in the basal plane formed after the most aggressive treatment described.

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