A simple method for graphene production based on exfoliation of graphite in water using 1-pyrenesulfonic acid sodium salt


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ABSTRACT

In this work we use a chemical approach based on supra-molecular and non-covalent interactions between graphene and 1-pyrenesulfonic acid sodium salt (Py–1SO3) to obtain a stable dispersion of graphene by using only water as solvent. The material has been characterized by a combination of spectroscopic and microscopic techniques. In particular, an extensive Raman analysis shows that we have \( \frac{\text{C}_2 \text{H}_7 \text{O}}{\text{C}_2 \text{H}_7 \text{O}} \times 70\% \) few-graphene layers (<7). We also show that the exfoliation efficiency strongly depends on the number of functional groups by comparing suspensions obtained by Py–1SO3 and 1,3,6,8-pyrenetetrasulfonic acid (Py–4SO3). A strong decrease in the exfoliation yield has been observed by using pyrene with 4 sulphonic groups (Py–4SO3), as compared to one sulphonic group (Py–1SO3). Being completely water-based, these suspensions can be used as inks for printable tattoo-based electro-chemical sensors.

1. Introduction

Graphene, a single-layer of graphite, has become one of the most exciting topics of research because of its outstanding optical, electronic and mechanical properties [1,2]. In particular, its optical transmittance (~98%) combined with high mobility makes graphene a perfect material for transparent conductive electrodes [3–5]. Few-layers thick graphene (less than ten layers) are being investigated with equal interest to monolayer graphene [6–8]. However, reliable production of single- and few-layers graphene samples in high quality and yield is still a challenge.

Liquid-phase exfoliation is a mass-scalable approach for the production of graphene [9–11]. However, this requires the use of organic solvents, which are expensive, toxic, difficult to remove and can cause environmental issues. Thus, an alternative chemical approach, which allows processability without affecting the intrinsic properties of graphene and makes use of “green” solvents such as water, is urgently required, in particular for life science applications.

The high surface energy of water does not allow dispersion and exfoliation of graphite in this solvent. Graphene can be produced in aqueous surfactant solutions [12]. However, the yield of the dispersed graphene flakes is low (<10%) and...
surfactants are difficult to remove [12]. A few recent works [13–17] report on the exfoliation of graphite through non-covalent interactions between graphene and pyrene derivatives, which can be seen as “nano-graphene units”. The aromatic core of the molecule allows its intercalation and physisorption on the hydrophobic surface of graphene through π–π interactions, while appropriate functional groups attached to the molecule allows the electrostatic stabilization of graphene in the solvent. Pyrene, as it is, is not soluble in water. Different groups can be attached to pyrene to tune its solubility such as sulphonic groups (SO3/C0) [13,15,16], carboxylic acid groups (COOH) [14] or more complex groups generating aromatic amphiphiles [17]. The nature and number of the functional groups is very important because the molecule must have a good affinity with the solvent, i.e. it needs to get sufficiently dissolved, but at the same time, the solvent has to allow hydrophobic interactions between graphene and the core of the molecule [14]. Thus, the easiest solution is to use a mixed solvent such as methanol and water: the first allows dispersion of the molecule in the solvent, while the second allows interactions between the molecule and graphene [13,14]. An overview of the most recent works is reported in Table 1.

In this work we investigate the use of 1-pyrenesulfonic acid sodium salt (Py–1SO3) to achieve exfoliation of graphite by using only water. The sulphonic group of this molecule improves the affinity of the molecule in the solvent, while at the same time hydrophobic interactions between graphene and the molecule are allowed. To the best of our knowledge, the use of Py–1SO3 for exfoliation of graphite has been reported only in the work of Jang et al. [13]. In this case, a mixed solvent was used. Furthermore, graphene was produced by using supercritical fluidic exfoliation, which requires high temperature and pressure, while Py–1SO3 was used to achieve non-covalent modification of graphene during exfoliation. Because of the complexity of this method, it is not possible to really get information on the role of Py–1SO3 as compared with the use of the solvent alone on the exfoliation mechanism and how this compares with the use of other pyrene derivatives.

In this work we aim at investigating the direct exfoliation of graphite in water using Py–1SO3 by using a combination of microscopic and spectroscopic techniques. In particular, we present an extensive Raman analysis of the material in suspension. A careful analysis of the Raman spectrum is very important since it is used to quantify the yield of single layers and to investigate the interaction between the molecules and graphene.

### 2. Experimental section

#### 2.1. Material preparation

The schematic of the exfoliation process is shown in Fig. 1. The Py–1SO3 yellowish solution was prepared by dissolving 1 mg of Py–1SO3 powder (Sigma–Aldrich, P97.0% (HPLC)) in 10 mL of distilled water. The dispersion was produced by sonicating (Bandelin DK 102P bath sonicator) 30 mg of graphite flakes (Bran Well UK, Grade: 99.5) with 10 mL of as-prepared Py–1SO3 solution. After 80 min sonication, the large cluster of non-exfoliated graphite can be removed by mild centrifugation at 1000 rpm for 20 min. The dispersion was then refilled with water and centrifuged at 12,000 rpm for 20 min for three times in order to wash the excess Py–1SO3. After washing, the graphene-based materials collected at

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### Table 1 – List of the works reporting production of graphene by chemical exfoliation of graphite with pyrene, as compared with our work. Details of the exfoliation process, the yield obtained and the Raman spectrum have been included (such as the shape of the 2D peak and the presence of the D peak).

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Molecule</th>
<th>Exfoliation process and yield</th>
<th>Raman Spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>[13]</td>
<td>Py–1SO3</td>
<td>Bath sonicator, mixed solvent</td>
<td>In most cases the 2D peak is not a single peak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mono and double layers (60%)</td>
<td>D peak is not shown, but D’ is visible</td>
</tr>
<tr>
<td>[14]</td>
<td>Py–COOH</td>
<td>Bath sonicator; mixed solvent</td>
<td>Single 2D peak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Single (&lt;10%) and few-layers</td>
<td>D peak: yes</td>
</tr>
<tr>
<td>[15]</td>
<td>Py–4SO3</td>
<td>Tip sonicator; deuterium oxide</td>
<td>G peak splitting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mostly single-layers</td>
<td>Single 2D peak</td>
</tr>
<tr>
<td>[16]</td>
<td>Py–NH2</td>
<td>Bath sonicator; water</td>
<td>D peak is not shown</td>
</tr>
<tr>
<td></td>
<td>Py–4SO3</td>
<td>Single-layers and bilayers</td>
<td>2D peak not shown</td>
</tr>
<tr>
<td>[17]</td>
<td>Amophilic–Py</td>
<td>Bath sonicator; mixed solvent</td>
<td>D peak: yes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Single layers and bilayers</td>
<td>2D peak: yes</td>
</tr>
<tr>
<td>This work</td>
<td>Py–1SO3</td>
<td>Bath sonicator; water</td>
<td>Single 2D peak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Single (~20%) and few-layers</td>
<td>D peak: yes</td>
</tr>
</tbody>
</table>
the bottom of the micro-centrifuge tubes were re-sonicated in water for 1 min. In the last step, the final dispersion was obtained after further removing the residual graphite flakes by mild centrifugation at 1000 rpm for 20 min. The resulting dispersion is gray and stable over months,

The film drying was carried out in air at room temperature for 3 days. The concentration of dispersion remaining after centrifugation is \( \frac{C_24}{0.074 \text{ mg/mL}} \), calculated using an extinction coefficient \( a_{660nm} = 2460 \text{ L g}^{-1} \text{ m}^{-1} \).

Suspensions obtained by chemical exfoliation with organic solvents (1-Methyl-2-pyrrolidinone, NMP) were also produced by following the recipe published in previous work [18,19]. We sonicated the dispersion for 3 days in order to achieve a high yield of single-layer graphene (50%) [18]. This type of suspensions has been already well characterized in previous works [18,19], so we simply use them as reference in order to compare the quality of the dispersions obtained with Py–1SO₃.

2.2. Characterization

A Perkin-Elmer λ-900 UV–vis-NIR spectrophotometer was used to perform UV–vis spectroscopy of the dispersion. Fluorescence measurements were obtained by using a Spex Fluorolog II, equipped with a 450 Watt Xenon lamp.

The prepared dispersion was drop casted on a SiO₂/Si substrate for Atomic Force Microscopy (AFM) and Raman Spectroscopy characterization. A Nanoscope (R) III a, operating in tapping mode was used. A Witec alpha300 Raman spectrometer, equipped with 488, 514.5 and 633 nm excitation lines and a piezoelectric stage for Raman mapping, was used.

The Raman peaks were fitted with Lorentzian lines. The laser power on the sample was below 1 mW in order to avoid damage of graphene and desorption of the molecules.

The flakes were also deposited by pipetting a few milliliters of the dispersion onto holey carbon mesh grid for Transmission Electron Microscopy (TEM) analysis. A FEI Tecnai F20 with 200 kV accelerating voltage was used.

The graphene laminates have been analyzed by Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS). A Thermo Scientific K alpha XPS was used with pass energy of 50 eV. The spot size on the sample is \( \sim 400 \mu \text{m} \). The XPS measurements were done on a vacuum filtered laminated (\( \sim 1.5 \mu \text{m} \) thickness, see Fig. 1C) that had been dried at room temperature for 2 weeks before the measurement.

3. Results and discussion

3.1. Flakes in suspension

Fig. 2 shows the absorption spectra of the Py–1SO₃ solution (bottom) and the Py–1SO₃/graphene dispersion (top). The spectrum of Py–1SO₃ solution shows the characteristic peaks between 200 and 400 nm [20]. Compared to the absorption spectrum of Py–1SO₃, the baseline of the absorption of the graphene-based dispersion absorbs over the whole frequency range, as it is expected for graphene dispersions [14]. The original peaks of the Py–1SO₃ solution are still visible, but they are broader: this is fingerprint of the π–π interaction between Py–1SO₃ and graphene, as observed when single-walled carbon nanotubes were dispersed by pyrene molecules [20,21]. Collectively, these observations confirm the presence of both pyrene and graphene, i.e. the molecules interact with the graphene sheets through π–π interaction, thus exfoliating

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**Fig. 1** – (A) Schematic of the exfoliation of graphite flakes using 1-pyrenesulfonic acid sodium salt (Py–1SO₃). The process includes different steps (mixing, exfoliation, and washing). The washing step is repeated for three times in order to remove the excess Py–1SO₃. (B) Digital picture of a vial containing the resulting graphene-based dispersion. (C) Py–1SO₃ based graphene film prepared by vacuum filtering dispersion.
and stabilizing graphene in water. Fluorescence measurements further confirm this result: the inset in Fig. 2 shows a strong decrease of the fluorescence after 1.5 h sonication. This is fingerprint of interaction between the molecules and graphene [22,23]. This type of charge transfer interaction is of great importance for the design of optoelectronic composite materials. In the case of composite materials based on graphene oxide, the nano-graphene molecules anchor on the functional groups on the basal plane causing the fluorescence to be fully quenched[24]. Note that in our case the fluorescence is not completely quenched. This means that there is an excess of molecules in solution. Indeed, we did try to perform Raman spectroscopy directly on the dispersion, but the Raman signal was completely hidden by a strong fluorescence background.

3.2. Flakes on the substrate

Raman spectroscopy is a powerful probe for characterizing graphene [25]. A typical Raman spectrum of monolayer graphene shows two main features [25]: the G peak, corresponding to the $E_{2g}$ phonon mode at the Brillouin zone center, at $\sim 1580$ cm$^{-1}$ and 2D peak, which is activated by two-phonons intervalley assisted Raman scattering, at $\sim 2700$ cm$^{-1}$. The 2D peak can be used to identify graphene [26]: the 2D peak is a single and sharp peak in the case of monolayer graphene, while in AB-stacked bilayer the 2D peak is composed by four bands. Graphite shows a broad and up-shifted 2D peak, which in first approximation can be fitted with two peaks. The 2D peak shape quickly evolves with the number of layers, so that the 2D band of a sample containing more than 8–10 layers is hardly distinguishable from that of bulk graphite [26]. In case of disorder, defect-activated features appear in the Raman spectrum: the D peak, first order of the 2D peak, which lies at $\sim 1350$ cm$^{-1}$, and the D’ peak, which appears at $\sim 1620$ cm$^{-1}$[27]. It is common for pristine graphene not to have enough structural defects for the D and D’ peaks to be Raman active so that they can only be seen at the edges [26,28].

In order to have a good statistics of the composition of the material obtained, Raman spectroscopy was performed on a large amount of flakes ($\sim 130$) deposited on a silicon substrate. We selected only flakes large enough to be observed under the optical microscope.

Fig. 3 shows the typical Raman spectra measured on our flakes. The spectra show common features of graphene, such as the G and 2D peaks. However, D and D’ peaks are also visible. A small peak at about 1245 cm$^{-1}$ also appears, Fig. 3. This is attributed to pyrene aggregates, since this peak has been observed in pyrene crystals [29]. Re-aggregation is driven by the amphilic nature of the molecules. Furthermore, a small fluorescence background is also visible in the Raman spectrum, indicating that the flakes are covered by a layer of molecules. Note that graphene is able to quench the fluorescence from the molecules due to charge transfer [30]. However, charge transfer happens only if the molecules are close enough to the surface of graphene [30]. In our case, since the fluorescence background is not completely quenched, we do expect to find a relatively thick layer of molecules on graphene.

Fig. 3 shows that the shape of the 2D peak strongly changes: this reflects the different thickness composition of the flakes. Based on the shape of the 2D peak, we can make an attempt to derive the amount of graphene in solution. We found that $\sim 18\%$ of the flakes are single-layers, $\sim 68\%$ are few-layer graphene flakes ($<7$ layers) and 14% are thick flakes. We used the same method to test stability against re-aggregation over longer time. We repeated the statistics on the same dispersions, which stand undisturbed for 8 months. About 130 flakes were checked. We found that the aged dispersion is composed by $\sim 22\%$ single-layers, $\sim 61\%$ few graphene layers ($<7$) and $\sim 17\%$ thick flakes. Thus, no appreciable difference is observed in the composition of the flakes after 8 months, demonstrating a good degree of stability. Note that these numbers need to be treated with care since the composition of the flakes on the substrate may not correspond exactly to the composition of the flakes in suspension. However, they offer a rough idea on the exfoliation efficiency. Note that both relative intensity and position of the 2D peak

![Fig. 2 – Absorption spectra of the Py–1SO$_3$ based graphene dispersion (top) and the Py–1SO$_3$ solution (bottom). (Inset) Fluorescence measurements of Py–1SO$_3$/graphene hybrids obtained with different sonication time.](image1)

![Fig. 3 – Representative Raman spectra taken at 2.41 eV of the flakes deposited on silicon.](image2)
cannot be used to identify graphene because they change with doping [31] and defects [32]. In contrast to mechanically exfoliated graphene, here we are dealing with flakes produced by chemical exfoliation, so we do expect doping and disorder to produce changes in Raman spectrum. For example, we do expect a shift and a decrease in the intensity of the 2D peak caused by doping from water (rather than from the molecules themselves) [33].

Furthermore, the Raman spectra show defects-activated features, indicating the presence of some form of disorder. Note that generally, in graphene dispersion the presence of a D peak is related to edges: for instance, NMP-based dispersions of graphene flakes with typical size of 10–20 nm show a strong D peak, which is not correlated with structural defects, but edges [18]. The similar effect could explain the D peak observed in our Raman spectrum. However, we observed the D peak to appear on both thin and thick layers and its intensity to strongly change from flake to flake. In addition to it, we did not observe any dependence on the intensity of the D peak with the sonication time: for increasing processing time, the size of the flakes should decrease, giving a higher D peak. We attribute the D peak to the presence of Py–1SO₃ molecules on graphene: since the molecules are nano-graphenes, once they are deposited on graphene, they break the symmetry of the basal plane, thus activating the D peak [15]. The intensity of the D peak will depend on the number of molecules and their configuration. This is in agreement with previous results obtained with other pyrene derivatives, where a D peak is always visible in the Raman spectrum, no matter the lateral size of the flakes [14,16,17], although its origin is not discussed. In order to investigate this idea, we selected two graphene flakes obtained by micro-mechanical exfoliation. 2 μL of Py–1SO₃ solution at 0.1 mg/mL were deposited on one of the flakes by drop casting. Then, we measured the Raman spectrum on both flakes with increasing laser power. It is expected that Py–1SO₃ will be desorbed at a certain laser power.

Fig. 4 shows the evolution of the Raman spectrum of Py–1SO₃/graphene with increasing laser power. At low power a strong fluorescence background is observed. However, the Raman features of graphene are visible, including a tiny D peak. For increasing laser power, the fluorescence disappears while the D peak is very weak. This probably corresponds to desorption of most of the molecules on the flake. Note that no strong variations in the G and 2D peaks width or position are observed. Above 3.5 mW of laser power the Raman spectrum strongly changes: a strong and broad D peak appears, indicating thermal degradation of the molecules-based film. Note that the D peak position does not correspond to the initial D peak position observed at low power. In the case of pristine graphene (i.e. without Py–1SO₃), no changes have been observed till ~7 mW, where a tiny D peak appears. Thus, particular attention has to be paid to the laser power in the Raman measurements of hybrid-graphene materials obtained with this method.

Because of the molecules residual on the flakes, AFM is not able to provide reliable information on the thickness distribution. A large amount of flakes (~62) were measured, but the smallest thickness was ~5 nm, well above 0.33 nm (theoretical thickness of a supported single-layer graphene), as expected. AFM also shows that the average lateral size of the flakes is 200–400 nm (Fig. 5). A few large flakes can also be found in the dispersion. These large flakes can be used to perform both Raman mapping and AFM on the same sample and thus compare the results obtained by the two techniques. Fig. 6A shows the AFM image of a large size flake. In addition the flake shows a folded part (in the dotted rectangle), useful to derive information on the distance between the layers. This figure shows that there are some small clusters on the flakes, visible also on the substrate. A few large
clusters are also visible. Fig. 6B shows that the thickness of the flake is about 5 nm and the distance between the two layers is again 5 nm. Fig. 6C shows the Raman spectrum measured in the center of the flake with a laser power of 0.7 mW: a few (2–3) layers 2D shape is observed. Note the presence of the pyrene peak at ~1245 cm\(^{-1}\), the fluorescence background and a small D peak. Since the flake is rather large, we do not expect edges to contribute to the D peak. This has been further confirmed by Raman mapping of the intensity ratio between the D and G peak, I(D)/I(G), on the flake. Fig. 6D shows that the maximum I(D)/I(G) is observed at the edges. However, far from the edges, I(D)/I(G) is not null and it is not uniform over the flake. This further confirms that the D peak cannot be entirely assigned to edges and disorder, but needs to be related to the amount and distribution of the molecules. Since we know that the molecules can be easily desorbed by laser heating (Fig. 4), we performed several Raman measurements in the center of the flake till we saw the fluorescence background disappearing. We then took a high resolution AFM image in the treated area, Fig. 6E. The topography image shows that the flake is covered by a rather uniform molecules film and a few clusters. However, the treated area (in the circle) seems rather clean-only several small clusters of ~20 nm in size are visible. The topography profile in Fig. 6F, corresponding to the line in Fig. 6E, shows that the thickness of the flake after laser treatment is ~1 nm, which would correspond to ~3 graphene layers, in good agreement with Raman spectroscopy. Note that the real thickness of the flake could be even smaller due to the presence of the molecules on the bottom side of the flake, in contact with the substrate. We have tried to remove this molecules film by washing the sample: we inserted 100 mL of water for 60 h and refilled the container with fresh water every 12 h. We then re-measured the same flakes after washing. We found that the excess molecules get removed further with each wash but a limit is reached at the 3rd or 4th wash, in agreement with Ref. [14]. Thus, the molecules cannot be completely removed. Plasma etching could be used, but this could damage the flakes.

Since the presence of free-molecules and aggregates can affect the efficiency of the exfoliation, we then prepared some dispersions with different concentration of Py–1SO\(_3\) (0.05 mg/mL, 0.1 mg/mL, and 5 mg/mL). At low concentration (0.05 mg/mL) the dispersion is mostly composed by thick flakes, as observed by optical microscope and Raman spectroscopy. As expected, by using high concentration (5 mg/mL), a large amount of molecules residual did not allow Raman measurements because the signal was hidden by a strong fluorescence. This lets us to conclude that a relatively large amount of Py–1SO\(_3\) is needed to achieve exfoliation. However, this concentration is probably close or higher to the critical concentration needed for the formation of small aggregates. This is also similar to what observed with surfactants, where a concentration very close to the critical micelle concentration is needed to achieve successful dispersion of graphite [12].

Finally, TEM analysis was performed to further characterize our dispersion, Fig. 7. TEM shows a large quantity of flakes.
with lateral size of ~200–400 nm, in agreement with AFM (Fig. 5). Most of the flakes are characterized by folded and wrinkled area, such as in Fig. 7A and C. This can further affect the thickness measured by AFM and contribute to the D peak intensity. In particular, by looking at the folded edges, the flake in Fig. 7A seems to be a large bilayer graphene folded on itself. The color contrast of the suspended part of this flake corresponds indeed to 3–4 layers. Some of the flakes are composed by many and disordered layers, which may indicate that these flakes are formed by re-aggregation during deposition on the TEM grid. Note that the TEM analysis is usually based on the color contrast of graphene. However, our flakes are covered with a large amount of molecules and this may cause a change in the contrast. This is for example visible in the thick layer in Fig. 7B, which is characterized by a non-uniform color, probably related to an inhomogeneous film of molecules.

3.3. Graphene laminates

XPS was performed in order to check that no graphene oxide or related version of derivatised graphene are present in our dispersion as well as to obtain the percentage of residual Py–1SO₃ after washing. Fig. 8A shows the survey spectrum recorded on the PSA-based graphene films. This reveals the presence of oxygen, nitrogen and sulfur with respective concentrations of 4.9, 0.7 and 0.8 at.%. Using the latter value, we can estimate that ~13% of the carbon signal is coming from the Py–1SO₃ molecule. The relatively high oxygen content is explained by the presence of SO₃ groups from the Py–1SO₃ molecule with a possible contribution from atmospheric adsorbates. These adsorbates are also probably contributing to the nitrogen peak too.

The carbon 1s spectrum of the Py–1SO₃ based graphene film is presented in Fig. 8B. No large peak between 286 and 288 eV, corresponding to C–O and C=O groups [34], is observed showing that our material does not contains graphene oxide. The C1s line is, on the contrary, very similar to the graphite signal with a slightly larger full width at half maximum (0.77 eV instead of 0.65 eV in graphite) which can be explained by the presence of the Py–1SO₃ molecules. The carbon 1s peak of the Py–1SO₃ based graphene film was fitted using the pristine graphite signal, the Py–1SO₃ powder signal and some residual C–O and CO bonds (~3%). Both graphite and Py–1SO₃ powder spectrum used here were recorded under the same conditions. A very good match is obtained using a Py–1SO₃ powder peak area equal to 14% of the total area which is in accordance with the Py–1SO₃ concentration calculated using the survey spectrum. Residual C–O and C=O bonds (~3%) could be attributed to the presence of contami-

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Fig. 7 – Selected TEM images of flakes prepared by Py–1SO₃ assisted exfoliation of graphite. (A) A few-graphene layers flake (probably a folded bilayers); (B) A thin (on the left) and thick (on the right) flake. (C) A folded and wrinkled flake: most of our flakes have folded and wrinkled area.

Fig. 8 – Survey (A) and carbon 1s (B) spectra of the Py–1SO₃ based graphene films. The C1s spectrum is fitted using the graphite signal (C–Cᵣ), the Py–1SO₃ powder signal (C–Cₚy–1SO₃), and C–O and C=O bonds.
nants and/or to a very slight oxidation. XPS measurements thus reveal that our method produces graphene films free from graphene oxide. We further estimate that around 13–14% of the carbon content in the film is coming from Py–1SO₃ molecules.

We also prepared NMP-based graphene laminate as described in Ref. [18]. The concentration of single-layer is expected to be ~50% [18]. Thus, we compared the Raman spectrum of this laminate with the one obtained with our Py–1SO₃/graphene dispersion, Fig. 9: first we can note a huge D peak in NMP-based graphene film (the Raman spectra have been normalized to the G peaks intensity). This is related to the different size of the flakes: sonication for 3 days strongly reduces the size of the flakes, compared to 80 min sonication of our method. A clear difference is visible in the shape of the 2D peak: this is a single and relatively sharp peak in NMP-based graphene paper, indicating the presence of randomly stacked graphene flakes. In contrast, the 2D peak of the Py–1SO₃ based graphene paper is composed by two components: one smaller, corresponding to the one observed in NMP based laminate, and one lying to higher wavenumbers. This reflects the thickness composition previously found by analyzing the flakes deposited on the substrate (Section 3.2).

3.4. Discussion

We found that by using our method, based on ultra-sonication with Py–1SO₃, it is possible to achieve stable graphene suspensions directly in water. It is now interesting to compare our results with previous works in order to achieve a further understanding of the exfoliation mechanism. In particular, it is interesting to compare exfoliation obtained with Py–1SO₃ and with Py–4SO₃. The difference between these two molecules is given only by the number of sulphonic groups. The presence of 4 sulphonic groups strongly improves the solubility of Py–4SO₃ in water. Thus, one would expect better exfoliation efficiency from Py–4SO₃ as compared to Py–1SO₃.

However, our results disagree with this expectation: Fig. 10 shows the suspensions obtained with Py–1SO₃ and Py–4SO₃. In the case of Py–4SO₃ the exfoliation yield is very small, as observed from the color of the suspension (almost transparent). On the other side, Dong et al. [15] and Zhang et al. [16] obtained a large yield of single-layers by using sonication with Py–4SO₃ directly in water, Table 1. However, the Raman spectra of the material obtained by the two group is very different: Dong et al. observed a clear splitting of the G peak [15], while Zhang et al. observed a very weak Raman spectrum, dominated by defects-activated peaks [16], Table 1. Thus, there is a large discrepancy in the results obtained by chemical exfoliation with Py–4SO₃ in water. This clearly shows that more studies on exfoliation of graphite by using pyrene derivatives are needed to get a deep understanding on the exfoliation mechanism. In particular, a detailed comparison of suspensions obtained with the same method, but using different pyrene derivatives would be really useful to understand the effect of the number and nature of the functional groups on the exfoliation mechanism. This knowledge can be then used to maximize the yield of monolayers.

4. Summary

We have developed a simple method to produce graphene suspensions by using non-covalent interaction with Py–1SO₃ using only water as solvent. We used a combination of different microscopy and spectroscopy techniques to study the material obtained. We have shown that exfoliation of graphite directly in water is quick, non-destructive and rather efficient. Our suspensions are produced in water with the help of low-cost and commercial molecules. Furthermore, since protein and other biological objects can be easily attached to pyrene, the suspension can be used as inks for printable tattoo-based electro-chemical sensors.

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