

Highly concentrated and stable few-layers graphene suspensions in pure and volatile organic solvents

Mohammad-Reza Azani^a, Azin Hassanpour^b, Veronica Carcelén^c, Carlos Gibaja^a, Daniel Granados^a, Ruben Mas-Ballesté^{b,*}, Felix Zamora^{a,b,*}

^a IMDEA-Nanoscience, C/ Faraday 9, Campus Cantoblanco-UAM, E-28049 Madrid, Spain

^b Departamento de Química Inorgánica, Universidad Autónoma de Madrid, UAM, E-28049 Madrid, Spain

^c Abengoa Research, Campus Palmas Altas, E-41014 Sevilla, Spain

ARTICLE INFO

Article history:

Received 8 October 2015

Received in revised form 5 December 2015

Accepted 7 December 2015

Keywords:

Few-layers graphene suspensions

Graphene powder

Graphite exfoliation

Conductive graphene coatings

ABSTRACT

Highly stable graphene suspensions in pure organic solvents, including volatile solvents such as ethanol, tetrahydrofuran, chloroform, acetone or toluene have been prepared by re-dispersion of a graphene-powder. Such re-dispersible solid is produced by precipitation or solvent elimination from graphene suspensions obtained by sonication of graphite in several organic solvent–water mixtures. Re-dispersion is feasible in a wide range of pure organic solvents, obtaining high quality few-layers graphene flakes stable in suspension for months. As a proof-of-concept, on-glass spray deposition of some of these suspensions, e.g. ethanol or tetrahydrofuran, results on electrically conductive transparent coatings. These results suggest industrial potential use of the scalable technology here developed to fabricate low-cost devices with many different potential applications.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene has attracted much attention as a new nano-carbon form with a unique structure and exceptional physical properties [1]. Commercial applications for graphene are expected in many areas from high-frequency electronics [2] to smart coatings [3]. While some of those applications will require coverage of large areas with single layer graphene of high structural quality, many others such as printed electronics [4], transparent electrodes [5] or conductive coatings [6] will demand low-cost graphene suspensions able to be processed by simple methods in large quantities and in a wide range of media. In this context, liquid phase exfoliation (LPE) of graphite is expected to fill this gap [7,8]. However, the preparation of graphene suspensions is still very limited. Probably the most promising LPE procedure is based on the graphite exfoliation using N-methyl-2-pyrrolidone (NMP) as solvent [9]. Despite having high quality graphene layers in graphene-NMP suspensions, the stability of the suspensions and even industrial scale-up [10], are the main drawbacks due to the features of NMP, which is a non-green solvent [11] with a high boiling

point that may prevent the processability of the graphene suspensions. Therefore, it seems obvious the need for the search of alternative solvents that could overcome these features. Following this idea, graphene dispersions in high boiling point solvents have been successfully transferred into volatile solvents by solvent exchange. However, these procedures yield to low concentration graphene suspensions [12]. In addition, a direct method based on sonication at very low power during long time of graphite in chloroform or isopropanol has allowed the formation of stable graphene suspensions with high graphene concentration [13]. Despite this interesting result, the long sonication time required to obtain the mentioned graphene suspensions limited the scalability of the process. Finally, recent reports showed the possibility of use mixtures acetone/water [14] and ethanol/water in graphite liquid phase exfoliation [15–17].

In a different approach, graphene suspensions have been obtained by reducing graphene oxide suspensions [18]. Although interesting, this is a not desirable strategy from different perspectives. In one hand, the atom economy of this approach is quite low which has a negative impact both environmentally and economically. On the other hand, commonly the physical properties of graphene are not completely restored after reduction of graphene oxide due to the defects produced in the chemical manipulation that results in a low quality graphene [19]. Thus, it is convenient to distinguish clearly those methods based on graphene oxide reduction and those that imply direct graphite

* Corresponding authors at: Departamento de Química Inorgánica, Universidad Autónoma de Madrid, UAM, E-28049 Madrid, Spain.

E-mail addresses: ruben.mas@uam.es (R. Mas-Ballesté), felix.zamora@uam.es (F. Zamora).

exfoliation, which up to this date implied the use of a limited number of solvents and working conditions that hampered its massive application.

In this work we have produced, by a simple two-steps procedure, graphene powders readily re-dispersible in water-free volatile organic solvents such as ethanol, tetrahydrofurane, chloroform, acetone or toluene. These graphene powders offer an unprecedented tool to obtain highly concentrated few-layers graphene suspensions in a wide range of organic solvents. The stability of these suspensions vs time has been evaluated showing an excellent performance. As a proof-of-concept of the potential applications of these suspensions, spray-on technique has been used to prepare transparent and conductive glasses.

2. Materials and methods

The starting commercial graphite source (NGS Naturgraphit) is based on natural graphite with particles sizes $<150\ \mu\text{m}$ (100 mesh) up to $<45\ \mu\text{m}$ (325 mesh). Solvents were provided by commercial sources and used without further purification unless is stated otherwise.

Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer 1650 spectrophotometer in KBr pellets. Optical absorption spectroscopy (OAS) was measured on graphene-ink suspensions using an Agilent 8452 diode array recorded over a 190–1100 nm range. Graphene-ink concentration, C_G , was determined from $A/l = \alpha C_G$, where A was measured at 280 nm. The absorption coefficient, α , which is related to the absorbance per unit path length, A/l , through the Lambert-Beer law $A/l = \alpha C$, is an important parameter in characterizing any dispersion. In order to accurately ascertain the graphene concentration, the absorption coefficient, α , is determined experimentally (Fig. S1). Therefore, the absorption coefficient was obtained by measuring the absorbance, the dispersion volume and weight of the dried graphene residue of a large volume of graphene dispersions in THF-water mixture (4:1) at different concentrations. Powder X-ray diffraction measurements were carried out using a diffractometer PANalytical X'Pert PRO theta/2theta primary monochromator and detector with fast X'Celerator. Transmission electron microscopy (TEM) images were obtained in a JEOL model Transmission Electron Microscope JEM 3000 F (field emission) with an accelerating voltage of 300 kV. Scanning electron microscopy (SEM) was performed using a microscope JEOL JM6400 equipped with a 40 kV microprobe. The substrates used for SEM were copper discs. Atomic force microscope (AFM) images were acquired in dynamic mode using a Nanotec Electronica system operating at room temperature in ambient air conditions. For AFM measurements, Olympus cantilevers were used with a nominal force constant of 0.75 N/m. The images were processed using WSxM software. All the samples of AFM were prepared with spraying the dilute suspensions of samples on SiO_2 . For AFM measurements previously distilled THF (tetrahydrofuran) was used. Raman spectra were recorded on a WITec/Alpha 300AR Raman confocal microscope at ambient conditions. The laser wavelength and power were 532 nm and 0.7 mW, respectively. Maps of Raman spectra of the entire graphene flakes were acquired to ensure the homogeneity of the flake. Thermal gravimetric analyses (TGA) were performed in a TGA TA instruments Q-500 analyzer. The temperature program was from 25 to 1000 °C, with a temperature rate of $5\ ^\circ\text{C}\ \text{min}^{-1}$ under a nitrogen flow.

Spray coating. The substrates were sprayed on glass substrates using a Meinhard TR-30-K1 nebulizer with a flow of argon 0.3 L/min. The film thickness can be controlled by spraying time and the suspension concentration. Transparency was measured at a wavelength of $\lambda = 550\ \text{nm}$ after annealing the conductive films at 350 °C for 15 min. Optical transmission spectra of the films

deposited on glass slides were recorded on a UV-vis spectrometer (Agilent 8452) with a glass slide as reference.

Sheet resistance measurements, R_s , were measured by a KDY-1 two-probe resistivity test system (GuangZhou KunDe) at 300 K on samples with contact made with graphite conductive paste at room temperature.

Determination of optimal solvent-water mixture. Graphene dispersion is prepared by sonicating 50 mg graphite in 10 mL of mixtures having different S:water (S = tetrahydrofurane, ethanol, acetone and acetonitrile) ratios, during 90 min at 310 W with 40 Hz, followed by centrifugation at $550 \times g$ for 60 min. Several ratios of S and water mixtures were explored to determine the optimum mixing S:water ratio (Table S1). The graphene concentration, C_G , was calculated by measuring the absorption at 270 nm, being the corresponding, experimentally determined, extinction coefficient $\varepsilon_{270\text{nm}} = 3180\ \text{L}\ \text{g}^{-1}\ \text{m}^{-1}$.

Preparation of THF-water suspension. 50 mg graphite were sonicated in 10 mL of THF-water (4:1) for 90 min at 310 W with 40 Hz, followed by centrifugation at $550 \times g$ for 60 min (named as suspension B). Table S2 and S1 shows conditions to form other suspensions. Different suspensions were obtained depending on centrifugation procedure (time and g force).

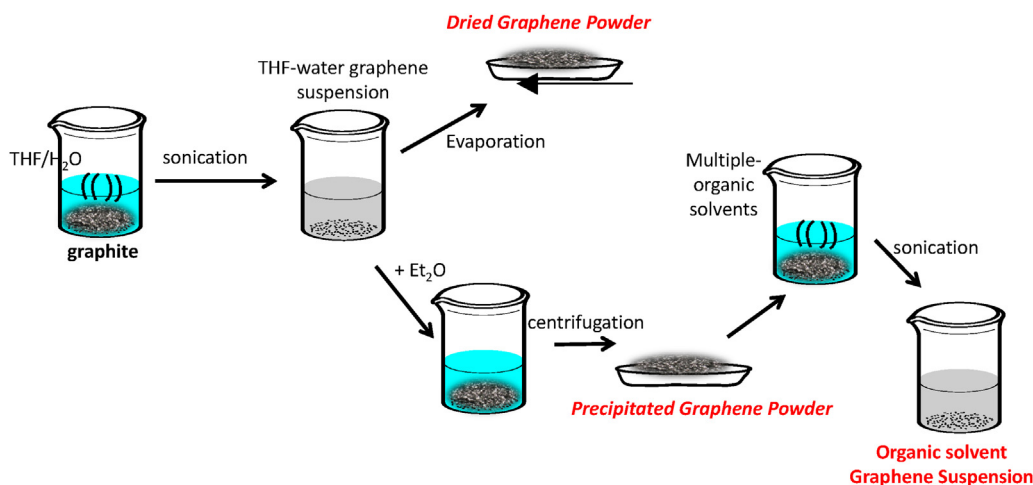
Preparation of graphene powders. The graphene suspension B was selected as starting material to isolate the so-called graphene powders. We have used two different experimental procedures: (i) *Dried graphene powder* is obtained upon complete vacuum dryness of a THF-water (4:1) suspension B. (ii) *Precipitated graphene powder* is isolated by adding diethylether to the initial THF-water (4:1) suspension provoking a fast precipitation of graphene powder. Addition of 1 mL diethyl ether to 4 mL freshly sonicated THF-water suspension B results in fast precipitation of a black powder that can be easily collected by using centrifuge with high speed ($16,000 \times g$ for 3 min) and washed several times with only distilled THF and then completely dried under vacuum.

Preparation of graphene suspensions in anhydrous media. *Dried graphene powder* and *precipitated graphene powder* can be re-dispersed in a variety of organic solvents including ethanol, tetrahydrofurane, chloroform, acetone or toluene. Typically, 1 mg of graphene powder was suspended in 10 mL of solvent, and sonicated for 90 min at 310 W, then the mixture was centrifuged at $550 \times g$ for 15 min. It is observed that the *precipitated graphene powder* is more efficiently re-dispersed than *dried graphene powder*. The concentration of graphene incorporated to the suspension was evaluated by UV measurements as in Section S1 (Tables S3 and S4).

3. Results and discussion

A general scheme of the whole procedure to generate high concentrated and stable graphene suspensions in pure volatile organic solvents is shown in Scheme 1.

A first step consists on initial liquid phase graphite exfoliation, which is optimal when sonication occurs in a mixture THF/ H_2O 1:4. Exfoliated graphene in suspension can be collected as solid powders (*vide infra*) which can be re-dispersed by sonication on several organic volatile solvents. In particular, in this work is shown that solid obtained by precipitation after addition of diethyl ether, affords higher graphene concentrations in suspension in a variety of pure organic solvents where direct exfoliation of graphite is not feasible. In addition, such precipitated graphene powder generates highly stable solutions that can remain unaltered over, at least, two months. Therefore, the isolation of a graphitic solid with a high degree of exfoliation (in particular the *precipitated graphene powder*) allows setting up protocols to prepare graphene suspensions in an unprecedented range of organic solvents.



Scheme 1. Summary of the experimental procedure used to produce few-layers graphene suspensions in a variety of pure organic solvents.

3.1. Starting THF–water graphene suspensions

In order to optimize the mixtures of organic solvent and water allowing the highest graphene concentration in suspension, several ratios solvent vs water were tested (Table S1 and Fig. S1).

Fig. S2 shows the UV–vis spectra and optical images of graphite suspended in a THF–water (4:1) mixture after sonication. As shown in Table S1 different graphene concentrations were reached by using several organic solvent–water mixtures. Pure water and pure organic solvents did not exfoliate graphite, while the use of an appropriate organic solvent mass fraction results on dark black graphene dispersions.

Typically, the UV–vis spectra observed for all organic solvent–water suspensions are comparable to the one shown in Fig. S2, which is mostly featureless, being the peak in the UV region the signature of the van Hove singularity in the graphene density of states [4]. The maximum yield obtained in our exfoliation experiments was found using a 4:1 THF–water mixture, which is several hundred times higher than that in pure water or THF and comparable to previously reported optimal values in N-methyl-2-pyrrolidone (NMP) [9] or other mixtures using ionic surfactants in water [20]. Interestingly, the exfoliation procedure reported herein takes only 90 min of sonication, which is considerably shorter than previous reported methods in which longer sonication times (ca. 8–9 h) were required to produce high concentration graphene suspensions [21]. In all cases, graphene suspensions were very stable at room temperature being the sedimentation less 20% after 3 months at room temperature. Other parameters such as the initial quantity of graphite, time and power of sonication, as well as centrifugal force (*g*) and time of centrifuge play key role in concentration, quality and quantity of the flakes in suspension [21]. After optimization of experimental setup, the lateral dimensions of the flakes were evaluated by atomic force microscopy (AFM) (Fig. S3) and transmission electronic microscopy (TEM) (Fig. S4), while the height of flakes were determined exclusively by AFM. Furthermore, thickness discrimination was achieved by adjusting centrifugation parameters (Table S2). Thus, the average thickness can be modulated from 12 nm (ca. 40 graphene layers), after applying $550 \times g$ centrifuge force during 60 min (suspension A), to 8 nm (ca. 20 graphene layers), by applying $4500 \times g$ for 30 min (suspension B), to 4 nm (ca. <10 graphene layers), by applying $16,000 \times g$ force during 10 min (suspension C). Higher centrifugal forces allows just the thinner flakes to remain in solution, which is attractive regarding applications such as transparent electrodes (*vide infra*), but also induces

a significant decrease of the graphene concentration. In fact, suspensions with flakes averaging 4 nm of thickness have a graphene content of 0.03 mg/mL. Raman spectroscopy (Fig. S5) supports the production of highly crystalline flakes with low defect content and non-appreciable amounts of oxidized functional groups.

3.2. Isolation and characterization of graphene powders

From the different initial graphene suspensions we have selected the so-called suspension B since shows a good compromise between the lateral dimensions (220 nm), thickness (8 nm) and concentration (Table S2).

An unreported feature found in this work is the fact that from the graphene suspensions obtained, a powder can be isolated and subsequently re-dispersed in a variety of pure organic volatile solvents where direct exfoliation was not achieved. This is a remarkable achievement because it makes possible to obtain few layers graphene dispersions in a wide range of media, conferring an unreported versatility to LPE techniques. Thus, the results reported herein can enable further implementation of graphene processing methods that make graphene-based technologies more accessible, technically and economically.

The isolated graphene powders show X-ray powder diffraction (XPD) that confirms their graphitic nature (Fig. S6). Additionally, Raman spectroscopic characterization of both graphene powders (Fig. S9) are almost coincident to that observed for the precursor graphene suspension B (Fig. S4). Fig. S9 plots typical Raman spectra of dried graphene powder and precipitated graphene powder deposited on SiO₂. The D band at ca. 1360 cm^{-1} is significantly larger than those of the starting graphite powder, indicating that the preparation process induces some structural defects. Such defects can be of two main types: basal plane defects and edge defects. Basal plane defects can generally result in an obvious broadening of G band, which is found in chemically reduced graphene which is not the case for the suspensions reported herein. In addition, both spectra show characteristic graphene features, G-band at ca. 1584 cm^{-1} and 2D-band ca. 2720 cm^{-1} .

Typical SEM images of the graphene powders are shown in Fig. 1 and S10. Interestingly, while no chemical/spectroscopic differences were observed between the two types of graphene powders, different morphologies were found depending on the precipitation method. On one hand, globular structures are observed for precipitated graphene powder. In contrast, laminar structures are found in the dried graphene powder. These observations suggest that

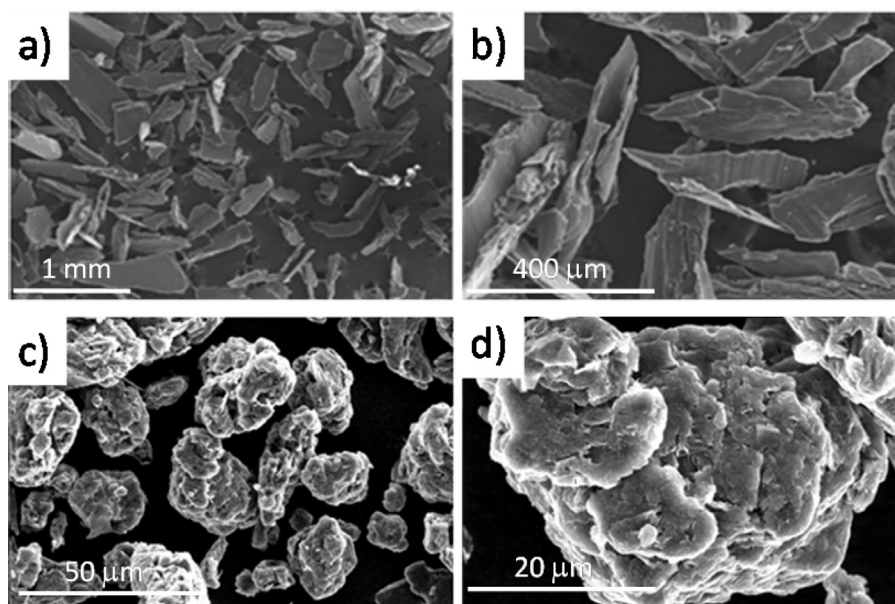


Fig. 1. SEM images of dried (a, b) and precipitated (c, d) graphene powder.

Table 1
Variation of the concentration (g/L) of precipitated and dried graphene powder re-dispersed in several organic solvents vs time.

Time (days)	Precipitated graphene powder			Dried graphene powder		
	THF	CHCl ₃	EtOH	THF	CHCl ₃	EtOH
0	0.08	0.10	0.09	0.04	0.07	0.09
3	0.05	0.10	0.06	^a	0.07	^a
5	0.04	0.10	0.05	^a	0.07	^a
25	0.04	0.10	0.03	^a	0.06	^a
60	0.04	0.10	0.03	^a	0.05	^a

^a Too low to be measured.

fast precipitation induced by adding an antisolvent prevents the re-aggregation, that otherwise occurs during solvent evaporation.

3.3. Graphene suspensions in pure organic volatile solvents

According to the procedure presented in the experimental section, new graphene suspensions were produced by re-dispersion of both graphene powders in several organic solvents (THF, EtOH or CHCl₃) using sonication followed by centrifugation. Graphene concentrations for fresh samples ($t=0$) and aged samples ($t=3, 5, 25$ and 60 days) are shown in Table 1. From a first inspection of the data at $t=0$, can be observed that precipitated graphene powder re-disperses more efficiently than the dried graphene powder. Thus, while initial graphene concentration achieved from precipitated graphene powder ranges from 0.08 to 0.1 g/L, the graphene content in solutions from dried graphene powder ranges from 0.04 to 0.09 g/L. More importantly, while precipitated graphene powder, affords very stable suspensions, the dried counterpart generates suspensions that sediments over time. Therefore, even if at $t=0$ the graphene content is significant for suspensions from dried graphene powder, it is likely that graphitic structures are rather stacked, resulting in a progressive sedimentation. Such loss of carbon material from the suspension scarcely occurs in solutions generated from precipitated graphene powder, probably because the graphene structures are smaller due to a more efficient delamination process. This explanation agrees well with images observed by SEM, which show stacked flat laminar structures from dried graphene powder but globular structures from precipitated graphene powder. SEM images suggest that re-aggregation is more efficient during the

solvent evaporation than in solid precipitation triggered by antisolvent addition and therefore, dried graphene powder is more difficult to re-disperse. It is worth to note that the results observed using CHCl₃ as a solvent indicate a remarkable stability of the suspension generated from precipitated graphene powder, which maintain an invariable concentration of 0.1 g/L from fresh samples to suspensions aged after, at least, 60 days.

Additional morphological TEM and AFM (Fig. 2, S11, S12 and S13) characterization confirm that the graphene flakes from precipitated graphene powder retain the lateral dimensions, thickness (ca. 5–6 nm) and morphology of the THF–water graphene suspension precursor. However, the height of dried graphene powder is significantly higher than the graphene precursor (from 8 nm to ca. 15 nm). This is in agreement with the lower stability observed for the suspensions generated by re-dispersion precipitated graphene powder.

3.4. Glass coating and electrical characterization

As a proof-of-concept of the potential use of these suspensions based on volatile organic solvents we have evaluated the efficiency of the suspensions formed with precipitated graphene powder in pure THF or ethanol to coat surfaces. For this purpose, we used suspensions from re-dispersed precipitated graphene powders in THF or ethanol and then centrifuged to produce suspensions with a graphene concentration of 0.03 and 0.02 mg/mL for EtOH and THF, respectively. The obtained suspensions were sprayed on glass and SiO₂ surfaces heated at 175 °C. In order to get a more homogeneous distribution of the graphene flakes on the substrate, annealing process (350 °C for 15 min) was carried out after deposition (Figs. S15–S17). The AFM and SEM inspection of the surfaces (Fig. 3) confirm a rather homogeneous coverage with graphene layers of lateral dimensions below 200–300 nm.

AFM topographic images were analyzed in order to determine the surface roughness of films generated by spraying precipitated graphene powder THF suspensions on glass substrates. A general inspection shows that the roughness significantly increase upon decreasing the level of transparency. Thus, at ca. 70% level of transparency the mean roughness is ± 20 nm while the mean roughness of the surface with 50% level of transparency increase up to ± 35 nm

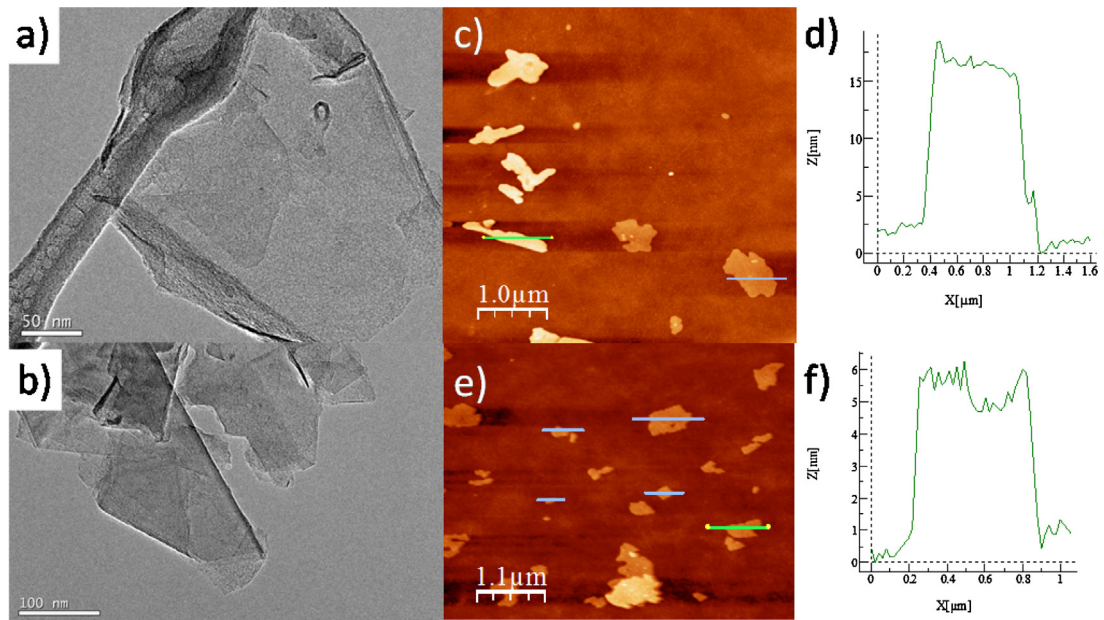


Fig. 2. TEM and topographic AFM images of dried graphene powder (a, c) and precipitated graphene powder (b, e). (d, f) Height profiles of the AFM images (c) and (e), respectively.

(Figs. S18 and S19). Additionally, the decrease of the transparency results on more heterogeneous surfaces.

The evaluation of the intensity ratio of I_D/I_G Raman signals of several flakes (Fig. 4) for re-dispersed precipitated graphene powder in pure EtOH or THF, are 0.5–1.0 and 0.4–1.1, respectively. These values are close to those found in the precursor THF–water graphene suspension, and suggest that re-dispersion in pure organic solvents do not implies a significant increase of defective structures in graphene flakes.

We examined the respective performance, transmittance vs sheet resistance of the sprayed graphene films at different levels of transparency going from 35% up to 70%.

The values of sheet resistance as a function of transparency are collected in Fig. 5. It is noteworthy that the sheet

resistance on surfaces with a level of transparency of 70% is close to values ranging between 70 and $130 \text{ k}\Omega \gamma^{-1}$ for glasses sprayed with graphene THF or EtOH suspensions, respectively. The value of $130 \text{ k}\Omega \gamma^{-1}$ compares well with other similar graphene experiments carried out depositing graphene suspensions [4] or reduced graphene oxide [22]. This value is still far from the best graphene-ink reported that shows $200 \text{ k}\Omega \gamma^{-1}$ with a transmittance of 90% using a non-volatile solvent as DMF. However, the use of the latter graphene-ink requires an annealing of higher than 400°C hampering direct applications based on direct deposition of the graphene suspension [23]. It is clear that by spraying a larger amount of graphene ink, we sacrifice the transparency however the conductivity significantly increased.

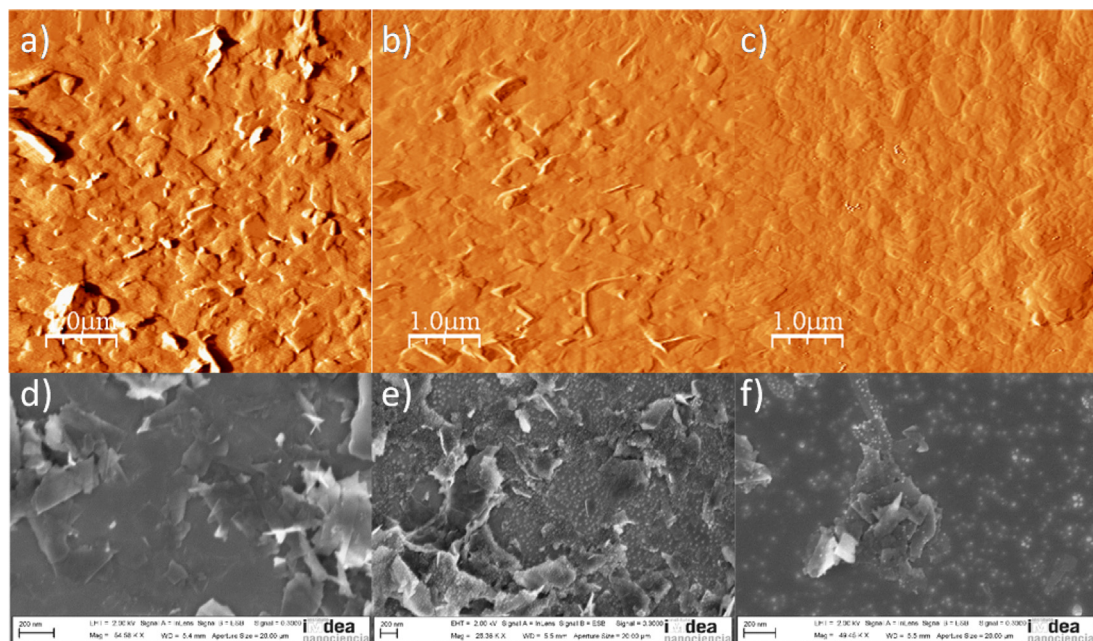


Fig. 3. AFM (a–c) and SEM (d–f) images precipitated graphene powder of EtOH suspensions sprayed SiO_2 surfaces after annealing at 350°C for 15 min with a coverage similar to a level of transparency 40%, 50% and 70%, respectively.

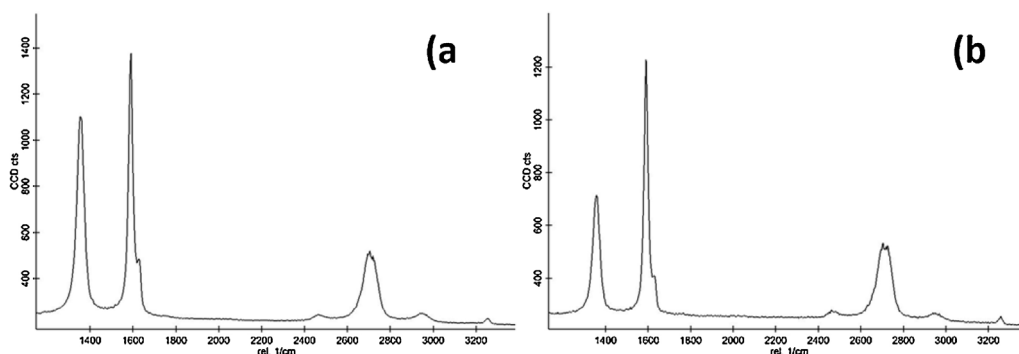


Fig. 4. Example of Raman spectra measured by depositing re-dispersed precipitated graphene powder on SiO₂ surface by spray method in pure (a) EtOH and (b) THF solvents.

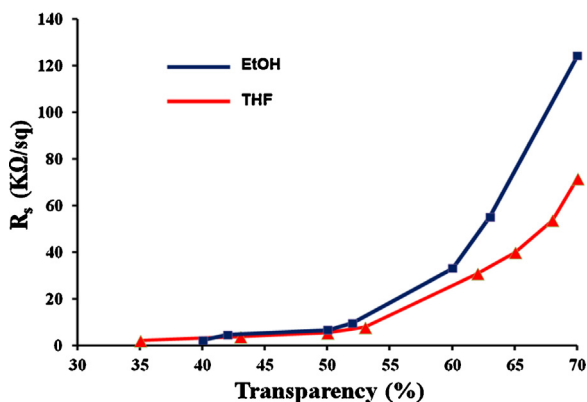


Fig. 5. Electrical characterization of transparent electrodes prepared from pure organic solvents suspensions of precipitated graphene powder. Sheet resistance vs transmittance for coated films with only THF or EtOH by spray method.

4. Conclusions

The simple preparation procedure here reported enables the possibility to obtain graphene suspensions in a variety of pure organic solvents (such as ethanol, tetrahydrofurane, chloroform, acetone or toluene). These few-layers graphene suspensions are formed from a graphene-powder isolated as a result of LPE of graphite in a mixture of water-THF. It is worth mentioning that the suspensions show high graphene concentrations in a variety of pure solvents where direct graphite exfoliation is not feasible, and they are very stable remaining almost unaltered upon standing at room temperature for 2 months. The morphological features of the suspensions consisting of few-layer high quality graphene flakes with lateral dimensions up to 500 nm and a nanometer thickness (*ca.* 6 nm) suggest that they are suitable to be sprayed on a variety of substrates. We showed a proof-of-concept application of these suspensions consisting of on-glass spray deposition of these graphene suspensions to produce electrodes with a good electrical conductivity vs transmittance ratio. The results obtained suggest potential applications for production of transparent conductive electrodes.

The results reported herein present several advantages with respect the state-of-the-art of graphene suspensions obtention by means of LPE. The present technology provides an efficient, scale-up and inexpensive method for the fabrication of graphene coatings and the possibility to produce graphene devices.

Acknowledgments

This research was financially supported by Abengoa Co., the Spanish Ministry of Economy and Competitiveness (MAT2013-46753-C2-1-P and RYC2012-09864) and Comunidad de Madrid (CAM 09-S2009-MAT-1467).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.apmt.2015.12.002](https://doi.org/10.1016/j.apmt.2015.12.002).

References

- [1] K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, A roadmap for graphene, *Nature* 490 (2012) 192–200.
- [2] Y.M. Lin, A. Valdes-Garcia, S.J. Han, D.B. Farmer, I. Meric, Y.N. Sun, Y.Q. Wu, C. Dimitrakopoulos, A. Grill, P. Avouris, K.A. Jenkins, Wafer-scale graphene integrated circuit, *Science* 332 (2011) 1294–1297.
- [3] L.B. Gao, G.X. Ni, Y.P. Liu, B. Liu, A.H.C. Neto, K.P. Loh, Face-to-face transfer of wafer-scale graphene films, *Nature* 505 (2014) 190–194.
- [4] F. Torrisi, T. Hasan, W.P. Wu, Z.P. Sun, A. Lombardo, T.S. Kulmala, G.W. Hsieh, S.J. Jung, F. Bonaccorso, P.J. Paul, D.P. Chu, A.C. Ferrari, Inkjet-printed graphene electronics, *ACS Nano* 6 (2012) 2992–3006.
- [5] H. Park, P.R. Brown, V. Buloyic, J. Kong, Graphene as transparent conducting electrodes in organic photovoltaics: studies in graphene morphology, hole transporting layers, and counter electrodes, *Nano Lett.* 12 (2012) 133–140.
- [6] J.B. Wu, M. Agrawal, H.A. Becerril, Z.N. Bao, Z.F. Liu, Y.S. Chen, P. Peumans, Organic light-emitting diodes on solution-processed graphene transparent electrodes, *ACS Nano* 4 (2010) 43–48.
- [7] V. Nicolosi, M. Chhowalla, M.G. Kanatzidis, M.S. Strano, J.N. Coleman, Liquid exfoliation of layered materials, *Science* 340 (2013) 1226419.
- [8] J.N. Coleman, Liquid exfoliation of defect-free graphene, *Acc. Chem. Res.* 46 (2013) 14–22.
- [9] Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z.Y. Sun, S. De, I.T. McGovern, B. Holland, M. Byrne, Y.K. Gun'ko, J.J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A.C. Ferrari, J.N. Coleman, High-yield production of graphene by liquid-phase exfoliation of graphite, *Nat. Nanotechnol.* 3 (2008) 563–568.
- [10] 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.M. 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.
- [11] C. Capello, U. Fischer, K. Hungerbuhler, What is a green solvent? A comprehensive framework for the environmental assessment of solvents, *Green Chem.* 9 (2007) 927–934.
- [12] X.Y. Zhang, A.C. Coleman, N. Katsonis, W.R. Browne, B.J. van Wees, B.L. Feringa, Dispersion of graphene in ethanol using a simple solvent exchange method, *Chem. Commun.* 46 (2010) 7539–7541.
- [13] A. O'Neill, U. Khan, P.N. Nirmalraj, J. Boland, J.N. Coleman, Graphene dispersion and exfoliation in low boiling point solvents, *J. Phys. Chem. C* 115 (2011) 5422–5428.
- [14] M. Yi, Z.G. Shen, X.J. Zhang, S.L. Ma, Achieving concentrated graphene dispersions in water/acetone mixtures by the strategy of tailoring Hansen solubility parameters, *J. Phys. D Appl. Phys.* 46 (2013) 025301.
- [15] X. Han, Y. Chen, H. Zhu, C. Preston, J. Wan, Z. Fang, L. Hu, Scalable, printable, surfactant-free graphene ink directly from graphite, *Nanotechnology* 24 (2013) 205304.
- [16] M. Yi, Z.G. Shen, S.L. Ma, X.J. Zhang, A mixed-solvent strategy for facile and green preparation of graphene by liquid-phase exfoliation of graphite, *J. Nanopart. Res.* 14 (2012) 1003.
- [17] W.-W. Liu, B.-Y. Xia, X.-X. Wang, J.-N. Wang, Exfoliation and dispersion of graphene in ethanol-water mixtures, *Front. Mater. Sci.* 6 (2012) 176–182.
- [18] B. Dai, L. Fu, L. Liao, N. Liu, K. Yan, Y. Chen, Z. Liu, High-quality single-layer graphene via reparative reduction of graphene oxide, *Nano Res.* 4 (2011) 434–439.

- [19] C. Gomez-Navarro, J.C. Meyer, R.S. Sundaram, A. Chuvilin, S. Kurasch, M. Burghard, K. Kern, U. Kaiser, Atomic structure of reduced graphene oxide, *Nano Lett.* 10 (2010) 1144–1148.
- [20] M. Lotya, Y. Hernandez, P.J. King, R.J. Smith, V. Nicolosi, L.S. Karlsson, F.M. Blighe, S. De, Z.M. Wang, I.T. McGovern, G.S. Duesberg, J.N. Coleman, Liquid phase production of graphene by exfoliation of graphite in surfactant/water solutions, *J. Am. Chem. Soc.* 131 (2009) 3611–3620.
- [21] U. Khan, A. O'Neill, M. Lotya, S. De, J.N. Coleman, High-concentration solvent exfoliation of graphene, *Small* 6 (2010) 864–871.
- [22] D. Kong, L.T. Le, Y. Li, J.L. Zunino, W. Lee, Temperature-dependent electrical properties of graphene inkjet-printed on flexible materials, *Langmuir* 28 (2012) 13467–13472.
- [23] J.T. Li, F. Ye, S. Vaziri, M. Muhammed, M.C. Lemme, M. Ostling, Efficient inkjet printing of graphene, *Adv. Mater.* 25 (2013) 3985–3992.