Enhancement of the DC electrical conductivity of Graphite Nanoplatelets through the control of the process parameters

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Abstract

Ever since its first obtainment as a single layer in 2004 through mechanical exfoliation [1], graphene and its related applications have received an ever growing attention, thanks to the peculiar properties of this material. Graphene mass production has recently become a crucial issue, in view of possible applications in various fields, such as flexible electronics [2], supercapacitors [3] and nanocomposites [4]. Among the different synthesis routes available, chemical exfoliation of graphene oxide (GO) and thermal exfoliation of graphite intercalation compounds (GIC) seem to be the most promising candidates for large yield production [5].

The work presented here is part of a larger study, whose main goal is to maximize the exfoliation yield of Thermally Expanded Graphite Oxide (TEGO) obtained starting from GIC (preferred over the liquid exfoliation route of GO, because of the simultaneous reduction of the material), and to tune the properties of the resulting graphite nanoplatelets (GNP) through the proper control of the synthesis parameters. GNPs are synthesized through thermal exfoliation of commercially available GIC, as reported elsewhere in detail [6]. The resulting TEGO is then dispersed in a suitable solvent mixture and the suspension is tip sonicated using an ultrasonic processor, thus obtaining GNPs. The sonicated GNP suspension is then subjected to vacuum filtration in order to obtain GNP thick films, having an average thickness in the range of 100-200 μm (depending on the sonication cycle and solvent used), suitable for electrical properties investigation.

Several process parameters are believed to be critical for the resulting physical and structural characteristics of GNPs. In our previous works we already carried out a systematic study of the influence of several parameters on the DC properties of GNP thick films. The investigated parameters include: i) GIC exfoliation temperature and process duration; ii) TEGO sonication duty cycle; iii) Temperature of the dispersion under sonication; iv) The solvent used for GNP dispersion. In particular the solvents investigated include acetone, N,N-Dimethylformamide (DMF), N-Methyl-2-pyrrolidone (NMP) and mixtures thereof. The previously investigated exfoliation temperature range goes from 750°C to 1250°C (an almost two fold increase of the DC electrical conductivity was found, as the GIC expansion temperature was raised from 750 to 1250°C [7]). The pulsed sonication cycle was preferred all throughout our research, in order to avoid overheating of the suspensions, and various cycles (differing on the ON and OFF duration of the process) have been considered. Finally the influence of the proper control of the suspension temperature during the sonication process has been addressed.

The study presented here aims at investigating the effect on the final DC electrical properties of the fabricated GNP films of several parameters, such as GIC exfoliation temperature, post-synthesis annealing temperature and type of solvent (DMF- or NMP-acetone mixtures). In particular the investigated GIC exfoliation temperatures are 1150°C, 1250°C and 1350°C setting the process duration at 5s. The TEGO sonication cycle was carried out using two different solvent mixtures, namely acetone:DMF and acetone:NMP, both at 9:1 volume ratio. Finally the effect on the DC conductivity of the GNP films of two subsequent annealing steps, carried out at 250°C and 350°C, was investigated.

After proper conditioning, as-produced GNP thick films, without metal coating, are characterized through electron microscopy, using a Zeiss Auriga FESEM. The obtained micrographs show a layered structure (Fig1(a)), demonstrating the high porosity of such films. It should be noted that only TEGOs collected from the top of the expansion crucible were utilized to produce the GNP films. In fact SEM analysis demonstrated that TEGOs collected from the bottom of the crucible are characterized by a blistered surface, due to entrapment of residual intercalating species in the gas phase (due to the poor heat exchange), as shown in Fig. 1(b) and confirmed by EDX (not shown). Fig 1 (c) and (d) demonstrate the absence of such blistering for GIC exfoliated at 1150°C and 1250°C respectively, whose corresponding TEGO have been collected from top of the crucible. On the other hand TEGO obtained at 1350°C 5s expansion, show the presence of pits (Fig.1(e)).

The DC sheet resistance of the GNP film is measured using the four-point probe method at room temperature, before and after each annealing step. The measurement is repeated by positioning the test-probes in six different configurations over the sample. Fig.2(a) shows the measured sheet resistances of the films fabricated in the different conditions (GIC exfoliation temperature and TEGO

sonication medium) and after each annealing cycles. The measured electrical conductivity of the produced films after the second annealing step is shown in Fig.2(b): the obtained values are in good agreement with data recently published in literature for few layer GNP-films [8]. Finally, the estimated porosity of the films shown in Fig.2(c) demonstrates the crucial effect of the solvent on the morphological characteristics of GNPs, as well as on TEGO exfoliation degree Such effect will be confirmed by statistical investigations, based on results of SEM and AFM analyses, on the lateral size and thickness of GNPs produced under the different conditions, as previously described.

References

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Figures

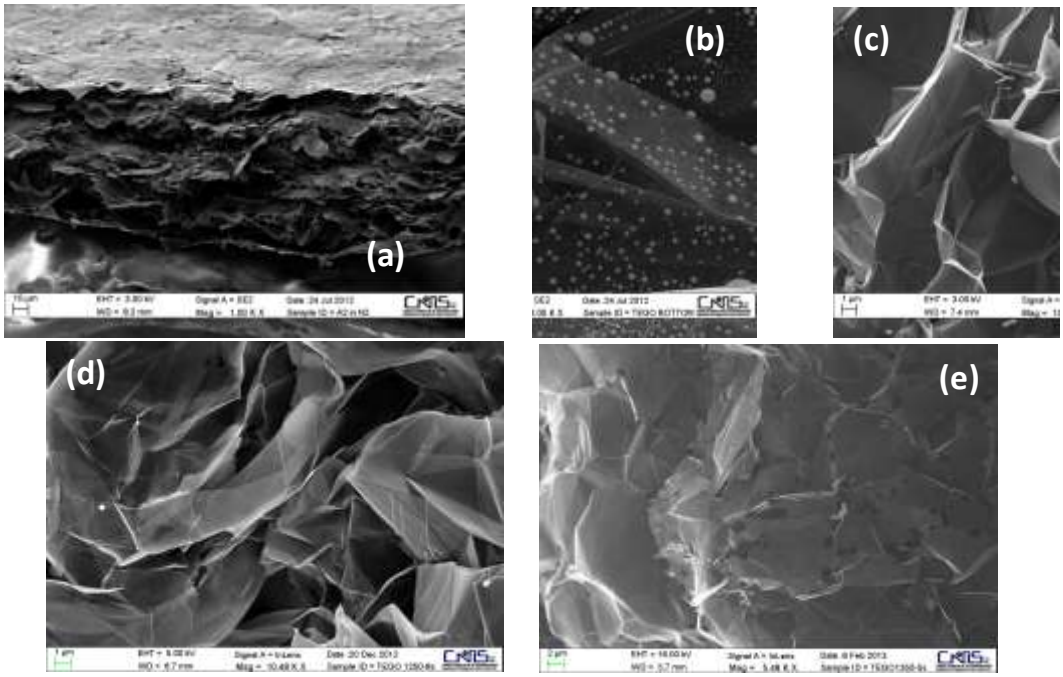

Fig.1 – SEM images of GNP thick film (a), and TEGO exfoliated at different temperatures and collected from the bottom (b) and top (c-e) of the crucible.

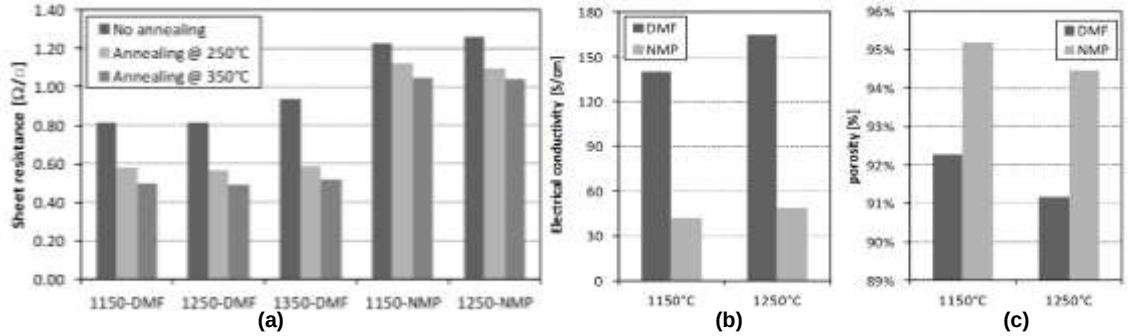

Fig. 2 – Measured sheet resistance (a), electrical conductivity (b) and porosity (c) of produced GNP thick films.