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Liquid-phase exfoliated graphene self-assembled films: Low-frequency noise and thermal-electric characterization

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ABSTRACT

In few years, graphene has become a revolutionary material, leading not only to applications in various fields such as electronics, medicine and environment, but also to the production of new types of 2D materials. In this work, Liquid Phase Exfoliation (LPE) was applied to natural graphite by brief sonication or mixer treatment in suitable solvents, in order to produce Few Layers Graphene (FLG) suspensions. Additionally, zeolite 4A (Z4A) was added during the production of FLG flakes-based inks, with the aim of aiding the exfoliation process. Conductive films were obtained by drop casting three types of suspensions over Al_2O_3 substrates with interdigitated electrodes, with total channel surface of 1.39 mm^2. The morphology characterization resulted in the verification of the presence of thin self-assembled flakes. Raman studies gave evidence of 4 to 10 layers graphene flakes. Electrical measurements were performed to state the Low-Frequency Noise and Thermal-Electric characteristics of the samples. We observe interesting relations between sample preparation procedures and electrical properties.

1. Introduction

Graphene represents a real 2D material, consisting in a single-layer of carbon atoms arranged in a sp^2 planar network with high specific surface area [1], unique electronic and mechanical properties [2] and high optical transmittance [3], [4]. Such features have enabled the development of new applications in different fields, such as flexible electronics and optoelectronics [5], [6], ultra-high frequency transistors [7], transparent electrodes for solar cells [8] and sensors [9], [10].

So far, different methods to obtain graphene have been developed, e.g. micromechanical exfoliation [1], thermal decomposition of hydrocarbon gases/liquids by Chemical Vapor Deposition (CVD) [11], [12], chemical exfoliation and Reduction of Graphene Oxide (RGO) [13]. Coleman and co-workers demonstrated that graphite can be exfoliated in the liquid phase, to get high quality graphene, with the aid of solvents [14–17]. In fact, it is possible to obtain FLG flakes using a sonication treatment, by matching the surface tension of solvent and that of exfoliated graphene [18]. It is worth to mention that, according to the state-of-the-art, the number of layers present in every flake should be less than 10 to be considered graphene [17], [19], [20]. Once the exfoliation is achieved, the main difficulty is to obtain a uniform and longtime stable suspension [16]. Some of the suspensions reported in literature present high entropy, making it difficult to classify the number of layers. Such suspensions are composed of populations of flakes with different sizes and thicknesses, and are usually called graphene inks [15], [21], [22].

The possibility to use graphene inks in specific electronic applications, such as conductive films and Field Effect Transistors (FETs), has motivated to study their behavior, in terms of 2D resistivity (ρ_{2D}) and Charge Neutrality Point (CNP), under specific variations of Electric and Magnetic Fields [23–26]. These studies have been addressed on Single Layer Graphene (SLG), Bilayer Graphene (BLG) and Few Layer Graphene (FLG) [13–26]. Nowadays, it is also important to study the behavior of macrostructure film devices made of interconnected individual graphene flakes, randomly ordered or self-assembled [27–29].

Low-Frequency Noise (LFN) described by the spectral density $S(f) \sim f^{-\gamma}$ (where f is the frequency and γ is the slope coefficient, usually $\sim$1), known as Flicker noise, has been used to determine whether the noise is generated by defects residing on the surface of electrical conductors or inside their volume [30–33]. In fact, recent

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Table 1
Summary of production parameters of the three different LPE-FLG suspensions.

Suspension denomination Process complete name		S_A 6h_NMP_TS	S_B 6h_NMP_Z4A_F	S_C 3h_NMP_Z4A_BS
Graphite/mg		20	2000	50
Initial Concentration		2 mg/ml	133 mg/ml	5 mg/ml
Solvent	Name	NMP	NMP	NMP
	Amount/ml	10	15	10
Zeolite 4A/mg	N/A	2000	50	
Sonication	Temp./°C	40	25	35
	Time/h	6	6	3
	Type	Tip	Mixer	Bath Sonication
Centrifugation	Velocity/rpm	3000	1000	1000
	Time/min	10	10	10
Deposition on Substrate	Amount/ul	2	2	2
	# Times	4	2	2
Temp. Dry/°C	Temp./°C	100	100	100
	Time/min	10	10	10

investigations on graphene, reported by Balandin et al. [31–33], have demonstrated that 1/*f* noise is merely a surface effect for conductive graphene films when the number of atomic layers $n_a < 7$ (thickness of $n_a = 1$ is 0.35 nm), otherwise can be attributed to a volume effect. Thus, 1/f noise remains an inevitable problem in new 2D materials, but also a potential tool to describe and compare the quality (in terms of defects) of graphene thin films.

In the present work, we present an original LPE method, which takes advantage from the addition of zeolite 4A (Z4A), to produce FLG flakes based inks. The FLG concentration was improved when the zeolite was added in the exfoliation procedure. Firstly, experiments were carried out to evaluate the performance of suspensions when the Z4A was introduced in the exfoliation phase. Subsequently, a comparative study of the electrical properties of three different suspensions was performed. We present Electrical Characterization (EC) and Low-Frequency Noise (LFN) measurements performed over these FLGs self-assembled films. Since the electric response to temperature changes is important for evaluating possible application areas of 2D materials, EC studies as a function of temperature are also presented and discussed.

2. Experimental

2.1. Materials

For the production of FLG suspensions, natural graphite powder (+50 mesh), purchased from Pingdu Huadong Graphite Co. Ltd, was exfoliated in 1-Methyl-2-pyrrolidinone (NMP) (purity 99%, from Sigma Aldrich (CAS: 872-50-4)), also in the presence of Zeolite 4A (Molecular sieve 4A, powder, activated, ~325 mesh particle size (CAS:70955-01-0)).

2.2. Exfoliation

We obtained graphene suspensions by different procedures. The first exfoliation (S_A) was carried out according to previous recipes [16], [18], [19]: 20 mg of graphite were exfoliated in 20 ml of NMP using a tip sonicator. Afterwards, the blend was centrifuged and the supernatant solution (80% of the solution) was recovered (see Table 1). In the second approach, we mixed graphite with zeolite 4A (Z4A) in order to improve exfoliation, maintaining a graphite/Z4A ratio of 1:1 (Table 1). We made exfoliation in the presence of zeolite following two different recipes. In the first (S_B), 2 g of graphite were mixed with 2 g of Z4A in the presence of NMP, and exfoliated using a mixer for 6 h at room temperature. Then, the solution was centrifuged at 1000 rpm, and the supernatant (80%) was recovered. In the second exfoliation with zeolite (S_C), a mixture of graphite and Z4A (50 mg each) in NMP was sonicated in a bath sonicator for 3 h, maintaining the temperature below 35 °C. Then, the solution was centrifuged at 1000 rpm, and also in this case the supernatant (80% of the solution) was collected.

2.3. Characterization

FLG self-assembled film samples were obtained by the drop casting technique on Al_2O_3 substrates with gold Inter-Digitated Electrodes (IDE1 and IDE2) ~1.3 µm thick, separated by a channel width of ~150 µm (Fig. 1d). The total channel area results to be ~1.39 mm^2. The films were characterized by the following techniques:

- SEM: the morphology of the FLG surface samples was studied by using a Field-Emission Scanning Electron Microscopy (SEM)

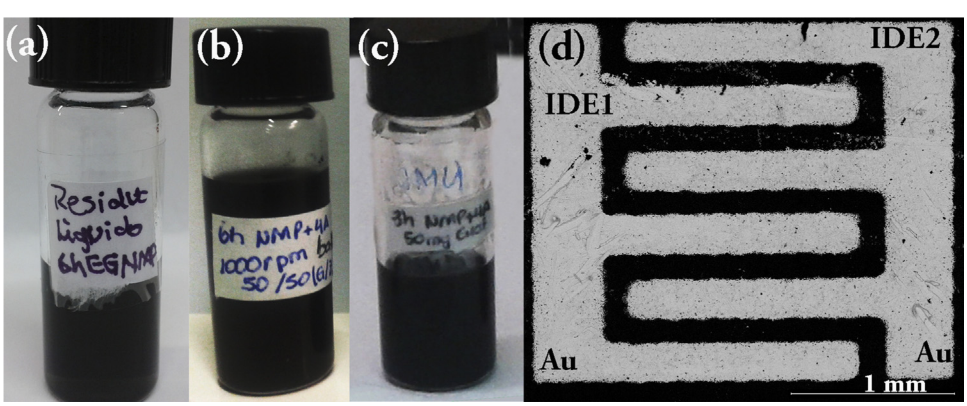

Fig. 1. Obtained exfoliated FLG suspensions: (a) S_A, (b) S_B and (c) S_C. (d) Sample holder (Al_2O_3 substrate and Au electrode contacts).

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