SYNTHESIS OF ZNO-NANOSTRUCTURES AND THEIR EFFECT ON THE DC ELECTRICAL CONDUCTIVITY OF GRAPHENE-BASED MATERIALS

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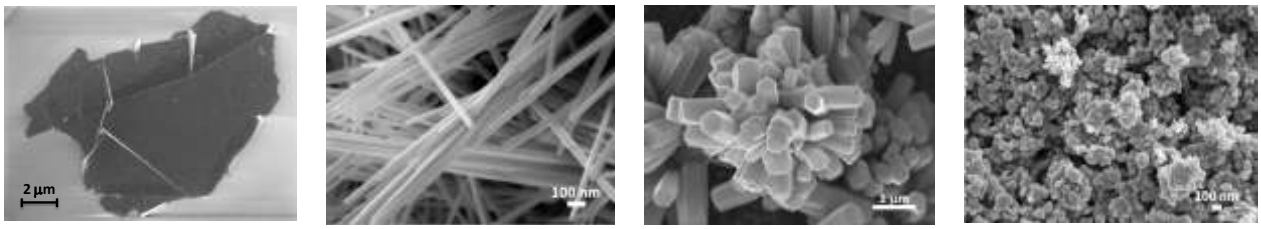
Zincoxide (ZnO) is a IIb-VI wide-band gap semiconducting material with a direct gap of 3.37 eV and a large exciton binding energy [1]. It crystallizes preferentially in the hexagonal wurtzite-type structure and forms variety of nanostructures. Having a wide range of versatile properties such as high transparency, piezoelectricity, chemical-sensing effects and doping dependent range of conductivity makes this material prominent for novel devices and applications [2]. Researchers have reported that when inorganic materials, such as zinc oxide, are integrated with graphene, their properties are greatly improved [3]. Moreover, ZnO nanostructures behave typically as n-type semiconductors, and hence they have the ability of activating electron-doping on graphene. Therefore, due to this effect, ZnO-nanostructures can offer to graphene-based nanomaterials additional functionalities, such as higher electrical conductivity, improved microwave adsorption properties, improved field emission [4-6].

In this work, we report the results of the research activity aimed at the synthesis and characterization of different types of ZnO micro/nano-structures, such as nanowires (NWs), microrods (MRs) and nanoparticles (NPs). The study has the final scope of producing new ZnO-graphene nanomaterials with enhanced electrical proprieties. In particular, in this paper we investigate the effect of different amount of ZnO micro/nano-structures on the morphology, sheet resistance and dc electrical conductivity of flexible foils made of graphene nanoplatelets (GNPs). The obtained results demonstrate that there exists an optimum weight concentration of ZnO micro/nano-structures over GNPs corresponding to a maximum enhancement of the dc electrical conductivity of the composite foil, thus suggeting the hypothesis of ZnO induced electron doping on graphene surface.

GNPs are produced by thermal expansion at 1150°C for 5 s of commercially available Graphite Intercalation Compound (GIC), as described in our earlier works [7]. ZnO-NWs, MRs, and NPs are synthesized through the process of thermal decomposition, hydrothermal method and sol-gel technique respectively [8-10]. Fig.1 shows the typical morphology of the produced nanostructures.



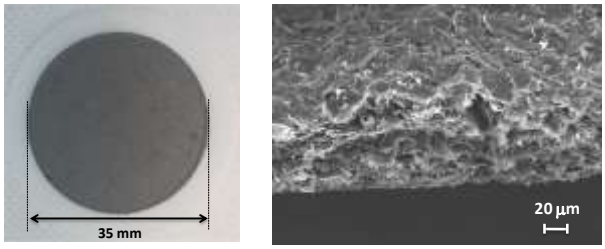
(a) A typical GNP flake **(b) ZnO nanowires** **(c) ZnO microrods** **(d) ZnO nanoparticles**

Fig.1. SEM images of nanostructures

GNPs have typical thickness in the range of 1-10 nm and lateral dimensions ranging from 1 up to 15 µm. ZnO-NWs and MRs are characterized by a typical hexagonal cross-section, with diameter of 20-40 nm and 200-500 nm, respectively, length up to 4 µm. ZnO-NPs have a quasi-spheroid shape with minimum and maximum diameters in the range 40-100 nm. After the growth, the ZnO micro/nano-structures are dispersed in acetone through tip sonication for 5 min and subsequently added to GNP-acetone suspension. The mixture solution is then further tip sonicated in order to achieve a uniform dispersion. Finally, the composite foils are obtained upon vacuum filtration of the prepared mixture suspension (Fig.2(a)). The hybrid thick films are subsequently dried at 120°C from

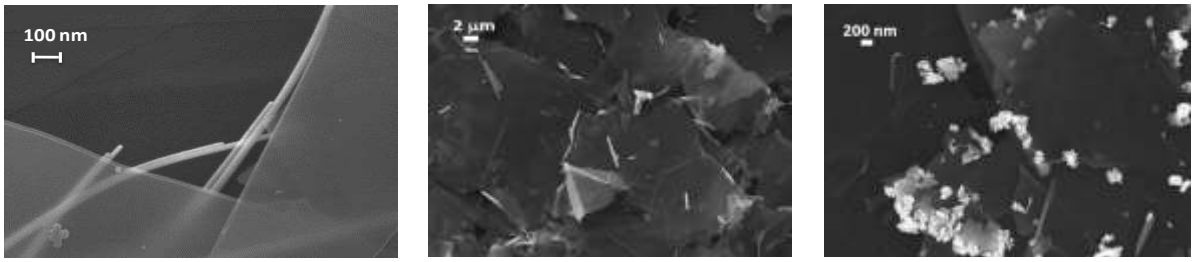
20 min, and then subjected to thermal annealing at 250°C for 3h to get rid of impurities and solvent residual. All composite foils produced are composed of 20 mg of GNP and an amount of either ZnO-NWs, or MRs, or NPs, ranging from 1 up to 20 mg.

The morphology of the produced nanomaterials is analyzed through SEM (Zeiss Auriga FESEM). From Fig.2(b), we observe that the fracture border of the composite foil has a stratified structure and that ZnO-NWs are quite uniformly distributed inside the material, with an increasing concentration from the top to the bottom of the foil. Sheet resistance (R_s) measurements are performed applying the four-point probe method, at room temperature, using a Signatone S301 stand, and Keithley 6221 dc/ac current source connected to a Keithley 2182a nano-voltmeter [11]. The film thickness (t), measured by using Mitutoyo 331-261 micrometer, is in the range of 90-120 µm.



(a) (b)

Fig.2. (a) Picture of a composite film (20 mg GNP and 2 mg ZnO-NWs) and (b) SEM images of its fraction section.



(a) (b) (c)

Fig.3. SEM images of top side of ZnO-GNP hybrid thick films made with nanowires (a), microrods (b) and nanoparticles (c).

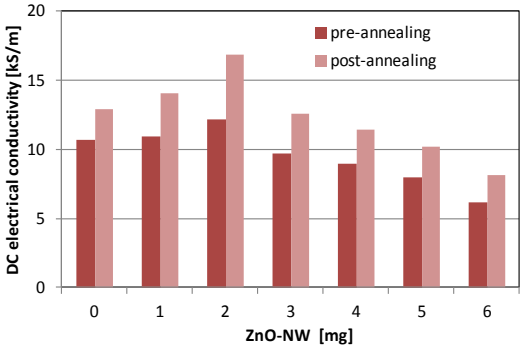


Fig.4. Electrical Conductivity measurements of the hybrid thick films loaded with various amounts of ZnO-NW and MR, before and after thermal annealing.

As an example, Fig.4 shows the measured values of the dc electrical conductivity of a ZnO-NW-graphene foil, before and after thermal annealing, as a function of the ZnO-NW amount. It is observed that the enhancement in conductivity for ZnO-NW loading up to 10% wt of GNPs can be explained considering that the ZnO-NWs, which are n-type semiconductors, may activate electron-doping on GNP surface [6]. A similar effect has been observed also in graphene-based composite foil made with ZnO-MRs or ZnO-NPs, but with different enhancement level, due to the different emission properties of different ZnO micro/nano-structures.

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