Synthesis of rGO/ZnO nanocomposites in ambient conditions

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Abstract

Due to its excellent electronic properties, graphene is a potential material for a new generation of gas sensors. However, graphene-related materials films do not have a good gas detection response. It has been shown that the addition of metallic or metals oxides nanoparticles improves the performance of this material. The objective of this work is to develop a fast and straightforward route for the synthesis of rGO /ZnO films for future applications in gas sensors. The rGO was synthesized by the modified Hummers method and the reduction process was carried out using laser radiation. ZnO nanoparticles were synthesized by the polymeric precursor's method, dispersed in acetone and drop-casted over the GO film. Raman spectroscopy and MEV demonstrate that drop-casting allows one to precisely control the amount of ZnO nanoparticles in the surface of rGO. Our results suggest that it was possible to tune rGO physical properties by drop-casting a ZnO nanoparticle dispersion in a rGO film.

Keywords: reduced graphene oxide; laser reduction; rGO/ZnO films.

Introduction

Graphene is a two-dimensional material that consists of a single layer of hybridized sp2 carbon atoms forming a hexagonal network arranged in the form of honeycombs [1]. Due to its excellent properties such as high electrical and thermal conductivity (5300 W/mK), high optical transmission (> 90%), high transport mobility (~ 2 x 10^5 cm^2/Vs), and high intrinsic surface area, it was shown that graphene is a potential candidate for applications as gas sensor material [1].

Several gas sensors using thin films of rGO have been reported. However, rGO sensors exhibit relatively poor detection response and long recovery times. It is well-known that the response of a semiconductor gas sensor is a surface phenomenon, so the decoration of the rGO surface with metallic nanoparticles (NPs) or metal oxide nanostructures (NSs) will affect the detection performance of these devices [2].

In recent years, rGO decorated with semiconductor metal oxides (SMOx), such In_2O_3, WO_3 and ZnO, showing superior gas sensing properties have been reported. ZnO is a group II-VI semiconductor with a gap of 3.3 eV and due to its remarkable properties, it is considered an important material for electronic and optical applications such as solar cells, energy storage devices and gas sensors. Within this context, rGO/ZnO nanocomposites has been studied, regarding its as capacitive and photoelectric properties [3]. On the other hand, the gas sensing properties of the rGO-ZnO nanocomposites have been little studied. The objective of this work is to develop a simple route for the production of rGO/ZnO films and their structural, compositional, and morphological characterization. Also, to determine whether one can finely tune the gas sensing properties of rGO by the addition of ZnO nanoparticles.

Experimental Procedure

Preparation of rGO / ZnO films

The GO was synthesized by the modified Hummers method. A solution containing graphene oxide (GO) was prepared by dispersing 1 mg of GO by ml. The solution was sonicated for 10 minutes and drop-casted on a 5 cm x 5 cm silicon substrate. The GO film with a thickness of ~ 3µm was then reduced by laser photoreduction. The GO films were irradiated, in their entire length, with an unfocused beam from the fourth harmonic (266 nm) of an 6 ns-pulsed Nd:YAG laser system with fundamental radiation of 1064 and fluency of 50 mJ/cm^2.

The ZnO nanoparticles were synthesized by the polymeric precursor method using zinc nitrate as the precursor metal. The ZnO nanoparticles were dispersed in acetone, forming a solution of 1.6 mg/ml. Then, a layer of this ZnO solution was drop-casted over the rGO surface. The results discussed here are labeled as rGO/ZnO_1 and rGO/ZnO_3, where 1 and 3 represent the number of drop-cast cycles of ZnO dispersion used to prepared the analyzed sample.

Results and Discussion

Figure 1 (a) shows the Raman spectrum of the rGO/ZnO_1 film and the inset presents the details of regions between 0 and 800 cm^{-1}. We can observe two intense peaks related to the D and G bands of rGO as well as a pronounced 2D band of the rGO. The bands observed in the vicinity of 500 cm^{-1} are related to the ZnO vibration modes.

The peak at 439.4 cm^{-1} is due to the vibrational mode of the E_2^{high} optical phonons that is associated with the vibrations of the O atoms. The band centered at 575.7 cm^{-1} refers to the longitudinal optical phonons E_1(LO); this mode is associated with defects such as oxygen vacancies or interstitial Zn atoms in ZnO. We can also observe the bands centered at 327.1, 383.3, 391.3 and 1141 cm^{-1} characteristic of this material. The ZnO spectrum also has two second-order bands. In the rGO/ZnO_1 spectrum of Figure 1 they appear centered at 647.9 and 1097 cm^{-1}, respectively [2].

Figure 2 presents XPS data of this rGO/ZnO_1 nanocomposite. Figure 2(a) shows the Survey and high-resolution spectra of the rGO/ZnO_1 film. It is possible to observe in the survey spectrum peaks at 1021.81, 531.81, 283.81 and 101.31, which refer to the electrons of Zn 2p, O 1s, C 1s and Si, respectively. This low concentration of Zn present in the rGO/ZnO_1 film is due to the low amount of the ZnO solution deposited on the film.

Figure 2(b) shows the high-resolution C spectrum of the rGO. The spectrum was deconvoluted into five bands referring to the C-C sp^2 (284.7 eV), C-C sp^3 (285.6 eV), CO (286.4 eV), C = O (287,6 eV) and COOH (289.6 eV). Figure 2 (c) shows the high-resolution spectrum of O that was deconvolved in three bands referring to three different oxygen species with binding energy at 534, 532.6 and 531.6 eV that refer to the O linked to ZnO/Si, O linked to C and O associated with poorly adsorbed species, respectively. Figure 2(d) shows the Zn 2p high-resolution spectrum. The image shows spectral lines in doublet with 1022.5 and 1045.7 eV binding energy for Zn 2p 1/2 and Zn 2p 3/2, respectively. These spectral lines are symmetrical and have ΔE = 23.2 eV[2]. This shows that the chemical status of the Zn^{2+} ions was not influenced by the presence of rGO.

Figure 3 shows the micrographs of the rGO and rGO/ZnO films with different layers of ZnO. In Figure 3 (a) and (b), it is possible to observe a smooth graphene oxide sheet with some folds due to the stacking of the sheets. In Figure 3 (c) and (d), we can observe the periodic and porous structure of the rGO formed during the reduction process. Figure 3(e)-(h) show the modification of the surface after the deposition of ZnO. It is possible that

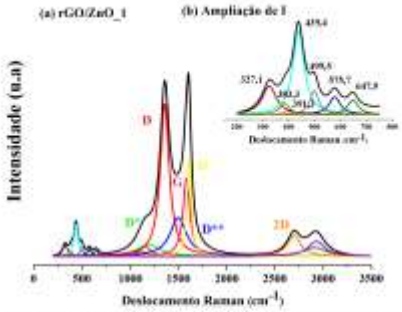

Figure 1 - (a) Raman spectrum of the rGO / ZnO film and (b) expansion of region I.

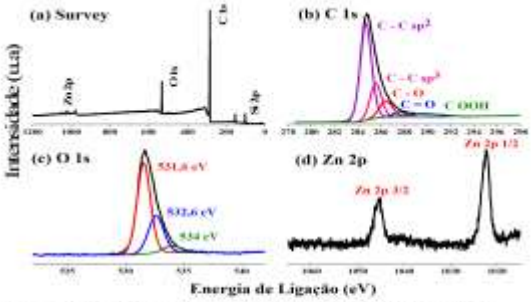

Figure 2 - XPS data (a) Survey spectrum of the rGO/ZnO film and high resolution spectrum of (b) C; (c) O and (d)Zn.

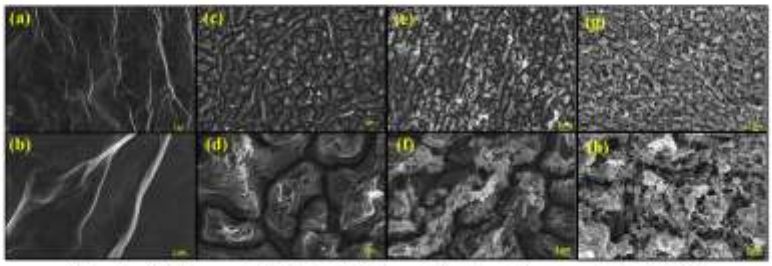

Figure 3 - SEM images with 5kX and 25kX magnification of films from (a) and (b) GO; (c) and (d) rGO and (e) and (f) rGO/ZnO_1 and (g) and (h) rGO/ZnO_3.

the drop-casting method allows precise control of the amount of ZnO nanoparticles, as by increasing the number of drop-cast cycles, the amount of nanoparticles also increase. It is important to mention that these particles are distributed over all the rGO surface and also the formation of some porous clusters With the increase in the number of ZnO layers deposited on the rGO film, the ZnO nanoparticles begin to cover the entire surface of the film and surround the rGO sheets.

Conclusions

Raman spectroscopy of the rGO/ZnO film shows the presence of the characteristic rGO bands (D, G and 2D) and some extra bands that refer to ZnO. XPS measurement detected the presence of a low concentration of ZnO in the rGO film due to the lower amount of ZnO deposited on the film. The high-resolution spectra of C1s and Zn2p are in agreement with the literature, there was no significant change in the bond energies or peak shape. SEM images show the periodic and porous structure of the rGO involved with the ZnO nanoparticles (spherical particles). Our results demonstrated that the procedure adopted in this work allows one to tune the amount of ZnO nanoparticles on the surface of rGO.

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