Chemical and morphological analysis of formation of rGO/ZnO composite obtained by microwave-assisted hydrothermal method

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Abstract. A chemical synthesis route for facile, fast and economical production of reduced graphene oxide/zinc oxide composites (rGO/ZnO) via a microwave-assisted hydrothermal method is presented. For a particular concentration (124 mM) of zinc acetate di-hydrate (Zn(CH3COO)2.2H2O) acting as precursor of Zn, different microwave irradiation times of the order of seconds were tested in order to select the more adequate time. Furthermore, with the selected irradiation time (40 s), different concentrations (31, 62 and 124 mM) were then considered and chemical and morphological properties of the obtained composites were evaluated. For their characterizations SEM, EDS, FTIR, Raman spectroscopy and XRD were employed. Experimental results confirm that the proposed synthesis route for the fabrication of rGO/ZnO is efficient, environmentally friendly and cost-effective.

1. Introduction
Graphene oxide-based materials represent an important area of research in materials science, as they have already been found to have promising applications in many fields [1],[2],[3],[4],[5],[6],[7]. The graphene oxide (GO) with hydroxyl and carboxyl groups owns excellent dispersibility in solvents and thus provides various opportunities for the fabrication of GO-based hybrid composites. It has a high surface/volume ratio, good adsorption capacity and allows the reduction of charge carrier recombination at the interface between the metal oxides and the reduced graphene oxide when a composite is synthetized with these materials. Zinc oxide (ZnO) has chemical and thermal stability, low cost, non-toxicity, biocompatibility and photoelectric and photoluminescent properties and is particularly promising in the degradation of organic compounds [8],[9],[10],[11],[12]. The notable properties of GO and ZnO lead to think about combining these materials to obtain hybrid materials with improved properties compared to the properties of their individual components [13]. These hybrid structures are especially alluring because exhibit additional advantages and synergistic properties that greatly augment their potential for many applications, such as photocatalysis, biomedical and gas sensing [14],[15],[16].

In most cases, the hybrid materials show a higher adsorption capacity, better UV and visible light
absorption, and a higher photocatalytic activity than the bare semiconductor, as well as better stability. Even though the number of publications related to the nanocarbon-semiconductor applications in photocatalysis has increased exponentially in the last 5 years, works of fundamental character to understand or design its operation were scarce in this period [17].

Now, the first step before these studies is the synthesis of the hybrid materials, which represents a challenging task in terms of controlled morphology and size [18]. For this reason, the microwave-assisted hydrothermal method (MAH) has been presented as an economical and efficient approach to produced hybrid composites, which offers uniform heating, high reaction rate, fast nucleation and crystal growth and reduction of graphene oxide without reducing agents [13],[19]. In this in-situ technique, the reduction of graphene oxide (GO) and formation of ZnO structures occur simultaneously, which results in high synthesis efficiency of rGO/ZnO composites.

In this work, we study the influence of the zinc precursor concentration and microwave irradiation time, on the morphological and chemical properties of hybrid composites. By increasing the precursor concentration, ZnO structures with different morphologies were successfully obtained; their size and the defect and disorder degree present in the GO network are affected by the microwave irradiation time. The study confirms that the proposed route for the synthesis of rGO/ZnO is efficient, environmentally friendly, cost-effective and appropriated for reproducibility of the results.

2. Experimental details
2.1 Materials
All chemicals used in the experiment were analytical grade. Graphite powder 20μm, Sulfuric acid (H2SO4, 98%), phosphoric acid (H3PO4, 85%), potassium permanganate (KMnO4, 99%), hydrogen peroxide (H2O2, 30%), Zinc acetate dihydrate (Zn(CH3COO)2.2H2O), Potassium hydroxide (KOH) and ethanol (C2H5OH) were purchased from Sigma-Aldrich and used as received. The aqueous solutions were prepared using ultrapure water obtained by Deionizer Nanopure Diamond Analytical Water System / Thermo Scientific D11901.

2.2 Synthesis of Graphene Oxide (GO)
The GO was prepared according to the Tour method that has been reported previously [20],[21]. First, a 9:1 mixture of concentrated H2SO4:H3PO4 (120:13.4 mL) was added to 1 g of graphite powder under stirring. Then, this mixture was heated to 50°C. After homogenizing the mixture, 6 g of KMnO4 were added slowly. The reaction continued at 50°C under strong magnetic stirring for 24 hours. Next, the mixture was cooled with 400 mL of cold deionized water (4°C) and 1.5 mL of 30% H2O2 was added slowly to stop the reaction. The graphite oxide produced was washed in multiple times with 2 M HCl aqueous solution and ultrapure water. Finally, the purified graphite oxide was easily dispersed in 400 mL of water by sonication with an ultrasound homogenizer, obtaining a light brown translucent dispersion of graphene oxide.

2.3 Synthesis of rGO/ZnO hybrid composites
Firstly, an aqueous solution of Zn(CH3COO)2.2H2O of known concentration (124 mM) was prepared under constant stirring. Subsequently, KOH solution (3 M) was added until a pH = 12 was attained. After that, a suspension of 10 mL of Zn(CH3COO)2 solution was submitted to ultrasonic treatment for 10 min and then it was added into the GO dispersion under magnetic stirring (previously synthesized by the Tour method). The final mixture was transferred into a Parr Microwave Acid Digestion Vessel and irradiated during different times of the order of seconds (22, 30, 40 and 90 s) on a microwave oven with a power of 1 kW. These samples were referred as GO/ZnO22, GO/ZnO30, GO/ZnO40 and GO/ZnO90. The precipitate powder was washed several times with deionized water and aqueous ethanol solution to
remove impurities. Finally, the powder samples were dried at 80°C for 7 h. The others GO/ZnO composites were prepared by employing a similar protocol but the zinc acetate concentration was varied as 15, 31 and 62 mM. These samples were referred as GO/ZnO$_{15}$, GO/ZnO$_{31}$ and GO/ZnO$_{62}$. The detailed reaction conditions are summarized in Table 1 and 2.

### Table 1. Designed conditions for the synthesis of different rGO/ZnO composites with various microwave irradiation times.

| Microwave irradiation time (s) | Zn(OAc)$_2$ concentration (mM) | pH  | GO volume (mL) | Zn(OAc)$_2$ volume (mL) |
|-------------------------------|---------------------------------|-----|----------------|-------------------------|
| 22                            | 124                             | 12  | 10             | 10                      |
| 30                            | 40                              | 90  |                |                         |
| 40                            | 124                             | 12  | 10             | 10                      |

### Table 2. Designed conditions for the synthesis of different rGO/ZnO composites with different Zn(OAc)$_2$ concentrations.

| Microwave irradiation time (s) | Zn(OAc)$_2$ concentration (mM) | pH  | GO volume (mL) | Zn(OAc)$_2$ volume (mL) |
|-------------------------------|---------------------------------|-----|----------------|-------------------------|
| 40                            | 62                              | 12  | 10             | 10                      |
| 31                            | 31                              | 12  | 10             | 10                      |
|

2.4 Characterization studies

Morphology of the composites was analyzed using a scanning electron microscope (SEM) JEOL JSM-6490LV endowed with an energy dispersive X-ray module (EDX) for performing the elemental composition analysis of the composites. Chemical group analysis of composites was evaluated using a Thermo Scientific Nicolet iS50 ATR-FTIR spectrometer with a wavelength range from 400 to 4000 cm$^{-1}$. Raman spectra at room temperature were recorded using a Horiba Jobin Yvon (Labram HR) Nikon (BX41) microscope and a 532 and 632.8 nm laser lines were used for excitation for GO and hybrid materials, respectively. The structural characterization was carried out using a X-ray diffractometer (XRD) D8 Bruker AXS equipped with a Cu-K$_\alpha$ source, $\lambda = 1.5406$ Å.

3. Results and discussion

3.1 Morphological analysis
The surface morphology of GO and rGO/ZnO composites were investigated by SEM analysis. Initially, the surface morphology of dry GO consists of overlapped large sheets. Its surface is relatively smooth although contains some slight wrinkles (Figure. 1a, b). On the other hand, different textures are noticed on the surface of rGO/ZnO hybrid composites irradiated with microwaves during different times (Figure. 2a-d). These consists of more corrugated and wrinkled sheets, and this can be attributed to two factors: (i) the presence of ZnO particles and (ii) the defects generated in the GO reduction process. It is clearly observed that the well-dispersed ZnO crystals are anchored onto the wrinkled rGO sheets via a rapid microwave irradiation times (22 and 30 s). However, with increasing microwave irradiation time (40 and 90 s), a better distribution and greater number of crystals is achieved, as a consequence of more time for the c direction to growth, in a similar way to that described by Barreto et al [22].
Under the same experimental conditions, except that varying the concentration of zinc acetate of 15, 31 and 62 mM, rGO/ZnO nanocomposites with different well-defined forms of ZnO were obtained for all cases. For 15 mM, ZnO like-flowers were obtained whose morphologies result from a particular configuration of several rods with sharp points deposited on GO flakes. The average length and diameter of rods in this case are 0.86 μm and 361.13 nm, respectively, as indicated in Figure. 3a-b. For 31 mM ZnO, rods with average length of 2.60 μm and average diameter of 511.54 nm, were obtained (Figure. 3c-d). Finally, for 62 mM ZnO, hexagonal ZnO rods with average length and diameter of 2.50 μm and...
406.08 nm, respectively, were obtained (Figure. 3e-f). For all cases, the ZnO structures were successfully deposited on the GO flakes. However, as expected, for the higher concentration of zinc acetate, there is a higher agglomeration of rods onto the GO flakes.

These results show the zinc precursor concentration is a key factor in the control of the size and morphology of ZnO crystals. Furthermore, hydrothermal and strong basicity conditions are favorable for the growth of ZnO along the c axis.

These ZnO particles are typically characterized by their aspect ratio (length divided by width). Rods with sharp tips conforming ZnO flowers have an aspect ratio of 2.4, ZnO rods obtained with a concentration of 31 mM have an aspect ratio of 5.1 and ZnO rods obtained with 61 mM have a aspect ratio of 6.8. This indicates that increasing the concentration of zinc precursor increases the aspect ratio of the particles, which is desirable in various applications as photocatalysis processes.

3.2 XRD analysis

X-ray diffraction patterns of the rGO/ZnO materials (Figure. 4) present characteristic peaks of the XRD pattern of the pristine ZnO, confirming that the wurtzite structure of the ZnO particles is maintained, as well as the presence of the GO. All major peaks clearly observed at 2ϴ= 31.8°, 34.5°, 36.3°, 47.6°, 56.6° and 62.9° correspond respectively to (100), (002), (101), (102), (110) and (103) crystalline planes of ZnO. The characteristic peak located at 2ϴ= 10.02° corresponds to (002) the crystalline reference plane of GO with an interplanar distance of 8.8 Å. The coexistence of the (002) graphite diffraction peak and ZnO diffraction peaks in rGO/ZnO XRD pattern indicates that ZnO particles have been anchored on the surface of the GO. As the microwave irradiation time increases (22, 30, 40 and 90 s), the characteristic peak of the GO corresponding to the plane (002) disappears, indicating that the degree of reduction is increasing of the composite material until reaching rGO.

Although XRD peak positions are identical for all samples, because chemical compositions are identical among them, intensities of each diffraction peak are different because the total area of each crystal face is not the same and the crystalline growth is anisotropic, as evidenced by the relative intensity ratios in Table 3. [23], [24]. Interestingly, the relative intensity ratios of the six main diffraction peaks with respect to the most intense peak (101) decrease when the microwave irradiation time increases; however, when the concentration of the zinc precursor increases, the relative intensity ratios increase. This suggests the establishment of interfacial interactions between ZnO crystals and rGO.

X-ray profile analysis is a simple and powerful tool to estimate the crystallite size (D). In this investigation D has been calculated from the full width at half maximum (FWHM) of (hkl) diffraction peak using Debye Scherrer’s formula and Williamson-Hall analysis using the Uniform Deformation Model (UDM) and the Uniform Deformation Stress Model (UDSM). In this calculation, the highest intensity (101) peak was considered and assumed to be Gaussian.

The average calculated crystallite sizes of ZnO being parts of hybrids is presented in Table 4. By comparing the values of average crystallite size obtained from all methods, it was found that the values are comparable and reasonable. In addition, these values are in accordance with those reported in the literature.
Table 3. Relative intensity ($I_i/I_0$) of the different diffraction peaks with respect to the most intense peak (101) for the rGO/ZnO materials.

| Miller index | $2\theta$ (degree) | rGO/ZnO$_{22}$ | rGO/ZnO$_{30}$ | rGO/ZnO$_{40}$ | rGO/ZnO$_{90}$ | rGO/ZnO$_{15}$ | rGO/ZnO$_{31}$ | rGO/ZnO$_{62}$ |
|--------------|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| (100)        | 31.8               | 0.69            | 0.68            | 0.64            | 0.62            | 0.59            | 0.58            | 0.65            |
| (002)        | 34.5               | 0.48            | 0.47            | 0.47            | 0.45            | 0.40            | 0.44            | 0.49            |
| (102)        | 47.6               | 0.15            | 0.24            | 0.19            | 0.19            | 0.22            | 0.18            | 0.24            |
| (110)        | 56.6               | 0.29            | 0.36            | 0.37            | 0.31            | 0.42            | 0.38            | 0.43            |
| (103)        | 62.9               | 0.23            | 0.28            | 0.30            | 0.24            | 0.32            | 0.31            | 0.37            |
| (101)        | 36.3               | 1               | 1               | 1               | 1               | 1               | 1               | 1               |

Table 4. Average crystalline size of the ZnO in rGO/ZnO materials for (101) peak using different analysis methods.

| Sample       | Scherrer's method | W-H method |
|--------------|--------------------|------------|
|              | UDM                | UDSM       |
| rGO/ZnO$_{22}$ | 18.38              | 25.43      | 20.71       |
| rGO/ZnO$_{30}$ | 21.60              | 24.78      | 18.82       |
| rGO/ZnO$_{40}$ | 21.55              | 21.03      | 16.47       |
| rGO/ZnO$_{90}$ | 18.59              | 27.21      | 24.16       |
| rGO/ZnO$_{15}$ | 29.51              | 70.44      | 28.41       |
| rGO/ZnO$_{31}$ | 21.41              | 26.18      | 19.85       |
| rGO/ZnO$_{62}$ | 29.98              | 57.82      | 28.99       |

3.3 EDS analysis
The Energy Dispersive X-ray Spectroscopy (EDS) was used for the local determination of chemical
composition of the samples (Table 5). EDS spectra and mapping of all samples confirmed the presence of zinc (Zn), oxygen (O), carbon (C) and potassium (K) elements. Other peaks in the spectra are due to the gold coating used for sample preparation. EDS mapping constitutes a qualitative assessment to evaluate the good homogeneity of the samples. The EDS spectrum and EDS mapping of the GO/ZnO₃₁ sample are presented in Figures 5 and 6, respectively.

In general, for all samples, it is observed that there is a considerable concentration of ZnO structures onto the rGO flakes. Also, a small percentage of traces of K is present, which was used to control the basicity of the solution. For the rGO/ZnO₂₂, rGO/ZnO₃₀, rGO/ZnO₄₀ and rGO/ZnO₆₀ samples, the highest atomic percentage of Zn is expected since the greatest amount of zinc acetate (124mM) was used. Although it would be expected that the atomic percentage of O should decrease by increasing the microwave irradiation time, since there is a greater probability of reduction, a greater number of ZnO crystals are also being generated. On the other hand, the atomic percentage of Zn for the rGO/ZnO₁₅, rGO/ZnO₃₁ and rGO/ZnO₆₂ samples as expected would increase, since the initial zinc acetate concentration was modified from 15, 31 and 62 mM. On the contrary, the atomic percentage of C decreases with increasing concentration of concentration of ZnO structures on rGO flakes.

![Figure 5 EDS spectrum of GO/ZnO₃₁ sample.](image)

![Figure 6 EDS mapping of GO/ZnO₃₁ sample.](image)

**Table 5.** Chemical composition of rGO/ZnO materials.

| Samples       | C   | O   | Zn  | K   | Totals |
|---------------|-----|-----|-----|-----|--------|
| rGO/ZnO₂₂     | 19,34 | 28,37 | 50,32 | 1,97 | 100    |
| rGO/ZnO₃₀     | 23,02 | 29,71 | 44,94 | 2,33 | 100    |
3.4 Raman analysis

Raman spectroscopy confirms the formation of GO and the hybrid structures. The Raman spectrum of GO, as shown in Figure 7, displays a D band at 1356 cm\(^{-1}\) and a G band at 1610 cm\(^{-1}\). The G band has to do with in-plane vibrations arising from the stretching of the C-C bonds of the sp\(^2\) hybridizations in graphitic materials. The D band, which is attributed to vibrations of the carbons with sp\(^3\) character and, hence, is an indicative of structural imperfections and induced defects during oxidation. The Raman spectra of the rGO/ZnO materials with various microwaves irradiation times (Figure 7a) show the characteristic D (1340 cm\(^{-1}\)) and G (1604 cm\(^{-1}\)) bands of the carbon-based materials. Similarly, Figure 7b shows Raman spectra of the rGO/ZnO materials with different zinc acetate concentrations with the presence of D (1339 cm\(^{-1}\)) and G (1596 cm\(^{-1}\)) bands too. The existence of the D and G bands in all samples indicates that during the decoration with ZnO structures onto the surface of rGO, the GO structures were not destroyed. The increase of the peaks intensity in all samples and the D band and G band shifted significantly regarding to GO suggests a significant interfacial interaction between ZnO particles and rGO is established [25-26].

![Raman spectra of GO and rGO/ZnO composites](image)

The intensity of the D band with respect to the G band (I_D/I_G) is typically used to characterize the level of graphitization (ordered structure) of these materials. As shown in Table 4, the calculated I_D/I_G ratios for GO, rGO/ZnO\(_{22}\), rGO/ZnO\(_{30}\), rGO/ZnO\(_{60}\) and rGO/ZnO\(_{90}\) show an increasing behavior of I_D/I_G as the microwave irradiation time increases, which suggests a greater structural disorder and defect sites on the rGO layers that can generate a strong interaction with ZnO structures. On the other hand, the rGO/ZnO\(_{31}\) and rGO/ZnO\(_{62}\) samples have the highest intensity ratios, which suggests that these are the hybrids with higher concentration of defects and therefore a greater anchoring of the ZnO crystals in the rGO sheets, as seen in the corresponding SEM micrographs and EDS analysis. In general, for all the hybrid materials obtained, the high I_D/I_G ratio evidences a high level of disorder, most likely denoting an advantageous integration of rGO with ZnO.
Table 6 I_D/I_G ratio of GO and rGO/ZnO hybrid materials.

| Samples       | I_D/I_G |
|---------------|---------|
| GO            | 0.84    |
| rGO/ZnO_{22}  | 1.529   |
| rGO/ZnO_{30}  | 1.744   |
| rGO/ZnO_{40}  | 1.708   |
| rGO/ZnO_{90}  | 1.855   |
| rGO/ZnO_{15}  | 1.548   |
| rGO/ZnO_{31}  | 1.938   |
| rGO/ZnO_{62}  | 1.943   |

3.5 FTIR analysis

FTIR studies were carried out to identify the chemical groups in rGO/ZnO hybrid materials. FTIR spectra in Figure 8 confirm their high hydrophilic character, as these show an intense broad band in the 3000-3678 cm\(^{-1}\) region due to the stretching vibrations of O-H groups. Furthermore, the spectra show the typical characteristic functional groups of GO based hybrid materials, alkoxy (C-O), aromatic (C=C) and epoxy (C=O=C) groups, corresponding to 1369, 1580 and 883 cm\(^{-1}\), respectively. The weak peak at 433 cm\(^{-1}\) corresponds to the \(E_{2}\) mode of hexagonal ZnO. As can be seen in all spectra, the typical C=O band of the GO does not appear, evidencing the reduction process and possibly an interaction between ZnO and rGO through the C=O groups.

![FTIR spectra of GO/ZnO composites with various microwaves irradiation times and different zinc acetate concentrations.](image)

Figure 8 FTIR-ATR spectra of GO/ZnO composites with various microwaves irradiation times and different zinc acetate concentrations.

4. Conclusions
In this research, rGO/ZnO composites were synthesized through microwave-assisted hydrothermal method considering four microwave irradiation times and three different Zn precursor concentrations. The chemical and morphological properties of the composites were studied using SEM, EDS, FTIR, Raman spectroscopy and XRD. After determining an adequate optimal microwave irradiation time to produce ZnO structures on the GO sheets, three concentrations of zinc acetate precursor were used aiming to obtain different morphologies of rGO/ZnO composites. Experimental results confirm the microwave-assisted hydrothermal method as a very useful technique to produce ZnO crystals successfully deposited on rGO flakes with morphology and size controlled. Furthermore, the microwave-assisted hydrothermal route minimizing the use of auxiliary substances (for example, solvents, separation agents), reducing costs, saving energy, short reaction times and avoiding the use of hazardous materials. Finally, these hybrid structures have great potential applications, particularly on green chemistry such as catalysts for reducing the environmental impact of agro-industrial waste and improving the quality and reuse of water.

5. References

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