Graphene oxide with the addition of different values of Ag nanoparticles.

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Abstract. In this work, the synthesis of graphene oxide (GO) were performed also we incorporate different Ag nanoparticles concentration with the aim to improve the properties of this material due to the assembled of metallic nanoparticles. In our case we choose Ag nanoparticles since that have a good reflectivity of light and the possibility to increment the Raman intensity by effects of the surface plasmon resonance. The synthesis of the GO and the Ag nanoparticles were achieved by the Hammers method and chemical reduction, respectively. Five samples of graphene oxide were obtained, with the addition of different values of Ag nanoparticles in those samples were 0 μL, 5 μL, 10 μL, 15 μL, y 50 μL. All samples were characterized by some spectroscopy techniques evaluating the absorption, structure and composition. We found that the Raman intensity increment for the sample of 15 μL of Ag nanoparticles, that effect could be related to the surface plasmon resonance of these nanoparticles.

1. Introduction

Graphene as a carbon material of only one atom of thickness and with a high surface area (~2600 m²/g), high chemical stability and unique mechanical and electronic properties [A method for the production of reduced graphene oxide using benzylamine as a reducing and stabilizing agent and its subsequent decoration with Ag nanoparticles for enzymeless hydrogen peroxide detection], by this way, it could be an ideal substrate for the anchoring of functionalized nanomaterials with applications in electrocatalytic or high-performance of electrochemical devices [1]. The growth of nanocrystals in graphene could have a higher rate of electron transport, a large electrolyte contact area, and structural stability. we have mentioned that graphene oxide (GO) is a basic material for the preparation of graphene in bulk quantities. Their surface functionalization with hydroxyl and epoxide groups in the plane, and carboxyl and carbonyl groups at the edges, in addition to their high solubility in water, are promising for many applications. [2,3]. Also, it has been proposed to functionalize the sheets of graphene oxide by inserting metallic nanoparticles to obtain a composite material. Metal nanoparticles play an important role in a large number of applications such as improved surface Raman scattering (SERS), visualization devices, catalysis, microelectronics, light emitting diodes, photovoltaic cells, as well as in medical applications and / or biological [4-5].
In fact, there are some papers about a biological application of graphene or its composites, however, these are relatively limited so the scientific community have recently been paid special attention in the antimicrobial activity. Recently, some studies have been reported on the synthesis of graphene nanocomposites with silver because it showed good antibacterial activity against Colibacillus, S. aureus and C. albicans, to mention a few. [6-7]. In some cases, the silver nanoparticles have been synthesized by the chemical reduction of AgNO\textsubscript{3} with PVP in a graphene suspension with an ethanol solution [8]. In this work, the synthesis of the GO and the incorporation of Ag nanoparticles were performed. Five samples of graphene oxide were obtained, the values of Ag nanoparticles added in the different samples were 0 μL, 5 μL, 10 μL, 15 μL y 50 μL. The results reflect an increment in the Raman intensity for the D and G bands of the Raman spectrum probably related to the surface plasmon resonance.

2. Experimental

2.1 Synthesis of graphene oxide
The synthesis of graphene oxide was carried out by the method of W. S. Hummers and R. E. Offeman [9]. For this, 2.0 g of graphite (0.166 mol) in 46 mL (0.86 mol), 95-99% sulfuric acid, H\textsubscript{2}SO\textsubscript{4}, is used with 1 mL (0.017 mol) of 85% phosphoric acid H\textsubscript{3}PO\textsubscript{4}; this system is placed in a cold-water bath at 4 °C, subsequently 6.05 g (0.038 mol) of potassium permanganate KMnO\textsubscript{4} is added slowly, it is left in agitation for 72 hours. After that time, 92 mL of distilled water are added; then add 15 mL of 30% hydrogen peroxide H\textsubscript{2}O\textsubscript{2}, leaving under stirring for 2 hours and finally at rest for 24 hours. The solid obtained is washed with abundant distilled water and the product is filtered, finally it was dried at room temperature and then proceed to its characterization.

2.2 Synthesis of Ag nanoparticles (AgNPs)
The solutions of AgNPs were prepared using 0.1 g of silver nitrate (AgNO\textsubscript{3}) in 100 ml of ethanol and 1 g of polyvinylpyrrolidone (PVP) as a stabilizing agent, with a weight ratio of 1:10 silver nitrate: PVP. The ethanolic solution containing the metal salt and PVP was refluxed at 363 K and stirred for 12 h [10]. The formation of AgNPs can be observed by a change of color in the solution, since the small AgNPs are amber. The addition of a small amount of PVP prevented the aggregation of Ag particles. Furthermore, the functionalization of the AgNPs was made in presence of a suspension of graphite oxide in ethanol, typically, a solution (2x10\textsuperscript{-3} Molar) of AgNO\textsubscript{3} in ethanol (calculated 1% w/ w with respect to the GO) was added slowly to a homogeneous suspension of graphene oxide under vigorous stirring.

2.3 Infrared spectroscopy by Fourier Transform (FTIR)
In the analysis of infrared spectroscopy a VARIAN 660 equipment was used, the software that was handled for the analysis of the samples was OMNIC. The spectra were acquired in transmittance mode performing 32 scans and with a resolution of 4 cm\textsuperscript{-1} in a range of 400 cm\textsuperscript{-1} to 4000 cm\textsuperscript{-1}.

2.4 Raman spectroscopy
The Raman spectroscopy analysis was performed by means of a Thermo Electron Spectrometer model Nicolet Almega XR. The spectra were obtained in the range of 400 to 4000 cm\textsuperscript{-1} with a total of 32 scans per spectrum, an opening of 25 μm for slit and a with the use of a laser of 633 nm as the excitation.

2.5 X-ray diffraction
X-ray diffraction (XRD) provides conclusive evidence of the oxidation reaction and the modification in the crystal structure of the initial graphite. The diffraction pattern was performed with a Brucker D8 powder diffractometer with Cu K\alpha radiation (\(\lambda = 0.154 \text{ nm}\)).
2.6 Atomic Force Microscopy
The atomic force microscopy (AFM) was performed in a Nanosurf easyScan 2 "isostage controller", using the easy Scan 2 controller, the images obtained were processed by Gwyddion software.

2.7 Transmission Electron Microscope (TEM)
Samples for TEM analysis were analyzed with a JEM-2010F FASTEM electron microscope operating at 300 kV. The samples were dissolved in ethanol and deposited on 300 mesh Cu grids, subsequently, the resulting samples were dried in air before being analyzed by TEM.

3. Results and discussion
The graphene oxide material was characterized by infrared spectroscopy (Figure 1) where the presence of the organic groups on the surface of the graphene oxide was confirmed. The characteristic bands of a highly oxygenated structure, a band around 1729 cm⁻¹ that corresponds to the stretching vibrations of C = O carboxylic groups, we also found a band at 1633 cm⁻¹ which corresponds to the link stretch vibration C = C due to the structure of graphite oxide, another band at 1065 cm⁻¹ corresponds to the characteristic vibration of the C-O ether group, in addition to the bands associated with the stretching and flexion vibration of the O-H bond around 3412 cm⁻¹ and 1403 cm⁻¹ respectively, the graphene oxide structure was sought as such in order to make the assemblies of the other materials. The silver nanoparticles were characterized by TEM transmission spectroscopy in order to be able to observe their same shape and size that can be seen in the figure 2.

![Figure 1. FTR-IR spectrum of the Graphene Oxide material. Presence of characteristic signals of the oxygenated groups as well as the presence of bands of carboxyl and hydroxyl groups and the C = C bond of the carbonaceous material.](image1)

![Figure 2. TEM images of the silver nanoparticles. They clearly indicate the presence and size of the particles, which consist of small NPs with sizes between 2-9 nm.](image2)

An analysis of X-ray diffraction for the GO material was made the Figure 3 shows 2 peaks, one located at 11° corresponding to signal C (001), which is very defined at angle values 2θ = 21.67° consequence of this is due to the possible incorporation of the functional groups in the graphite plane, has a slight displacement that could be attributed to higher C / O ratio present in the sample due to a distortion of the network difference of pure graphite. Also, some disordered structures present in the sample that move away from the crystallinity as the part of the oxygens, have a peak at 2θ = 43.01° that correspond to the C plane (001) regions that remain oxidized and reduced (H-GO) the interplanar distance for this point is d (002) = 0.38 nm impurities in the material that also affect the measurements and comparisons with the diffractograms already established in the literature. Applying the Bragg equation to the diffraction peak located at 2θ = 11° gives a value of
7.6 Å, which would indicate an increase in the interplanar distance (002) compared to the initial graphite.

Once the presence of the structure for GO has been confirmed, as well as the silver nanoparticles obtained, the functionalization or assembly of both materials is proceeded. With the motive of obtaining an improved nanomaterial in its physical and chemical characteristics, it is known that by itself these materials have specific functions and applications in different sectors, so with this union the idea is to improve and make the material more effective to give better results in the use and application of it, as the first point the X-ray diffraction spectrum initially had a diffraction pattern that had 2 peaks at 2Θ at 11° and at 43.01° indicating the presence of GO material recorded on the plane with C signal (001). After carrying out the functionalization with the silver nanoparticles (Figure 4), the peak located at 43.01° shows a signal variation that indicates the presence of metallic nanoparticles in the GO-Ag system, two more peaks at 35° and at 26° are also observed, suggesting the stabilization of the sheets of GO that is possibly due to the incrustation of the silver nanoparticles in the carbonaceous structure.

On the other hand, the appearance of a deformation or widening of the peaks at 26°, 35° and 43.01° indicates a restoration of the sp2 hybridization, which is attributed to the fact that the nanoparticles contribute in the reduction of GO.

![Figure 3. DRX spectrum of Graphene Oxide material. Carbonaceous structure, material with presence of oxidized regions and reduced signal of an oxidized carbonaceous plane.](image)

![Figure 4. DRX Diffraction Spectrum of the GO-Ag system. Functionalized nanoparticles on the GO matrix.](image)

To give us a better idea of the interaction between GO matrix with the silver nanoparticles, an AFM spectroscopy was performed. Figure 5 shown the presence of agglomerations of nanoparticles, which could contribute in the DRX patterns with a weak signal corresponding at the plasmon faces (111), however it are less intense than faces (220) probably due to an alteration or growth of nanoparticles on the surface of graphene oxide. Once the metallic nanoparticles are functionalized, the surface is more unstable or rougher, demonstrating the presence of nanoparticles with a size of <9 nm which could be ideal for the desired results since the smaller the material tends to show better results, but not only that observe also there are larger particles the clusters or agglomerates more visible and somehow protruding with respect to the nanoparticles of lower proportion.
To achieve remarkable results, we opted to vary the concentrations of the silver nanoparticles in terms of the deposit on the matrix of the GO and it was preceded to perform a Raman spectroscopy. In figure 6, we show the optimum level or a suitable concentration for the improvement of the quality of the samples. We found that a high concentration of nanoparticles has an optimal in 15 μL, as we could see the intensity does not increase more than expected, there is a better intensity with a minimum level of nanoparticles, which leads us to the conclusion that the more deposited the sample becomes saturated and loses the improvement in the characteristics, in this case the Raman intensity. These results are excellent candidates for the biological part since there is a notable improvement in the D band of the GO material which is characteristic of the presence of oxygenated material and ideal for a bactericidal material.

Figure 5. AFM of the graphene oxide surface functionalized with silver nanoparticles.

Figure 6. Raman spectrum of the GO-Ag functionalized material. Variation in silver nanoparticle concentrations.

4. Conclusions
An important aspect that has been presented is the characterization of the AgNPs and the GO material since it is a fundamental process to evaluate the preparation of that materials and their properties. By means of these techniques we can obtain structural information (XRD, RAMAN ...), morphology (TEM), allowing us to know when the synthesis process has concluded and evaluate the quality of the batch of AgNPs and GO prepared. These techniques also give us knowledge to propose the type of applications. When functionalizing GO with silver nanoparticles the characteristics of these materials change and show an improvement in structure and composition, the presence of AgNPs on the surface of the GO give the presence of free electrons in the
conduction band, which induces a collective excitation of these electrons and as a consequence a strong interaction with the incident light, that effect could be applied for biosensors or biological markers. On the other hand, the improved intensity on the Raman spectrum could be explained as an increase in the vibration of the sample by the surface plasmon resonance, which could improve the use of this material in the biological applications, the D band shows a remarkable growth and this is characterized to the vibrations of organic bonds as presence of oxygen and with this the material can be use for bactericidal applications, since the function would be reflected in the bacterial death by a possible oxidative stress inside the bacterium.

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