SILVER NANOAGGREGATES ON CHITOSAN FUNCTIONALIZED REDUCED GRAPHENE OXIDE USING MICROWAVES RADIATION

IOSODY SILVA-CASTRO[1]**, PABLO MARTÍN-RAMOS**[2]**,
MERCEDES SÁNCHEZ-BASCONES**[3]**, LUIS M. NAVAS-GRACIA**[1]
and JESÚS MARTÍN-GIL[1]

[1]Department of Agriculture and Forestry Engineering
ETSIIAA, Universidad de Valladolid
Avenida de Madrid 44
34004 Palencia
Spain

[2]Department of Agricultural and Environmental Sciences
EPSH, University of Zaragoza
Carretera de Cuarte
s/n, 22071 Huesca
Spain
e-mail: pmr@unizar.es

[3]Department of Agriculture and Forestry Science
ETSIIAA, Universidad de Valladolid
Avenida de Madrid 57
34004 Palencia
Spain

Abstract

A reduced graphene oxide (rGO)/chitosan oligomers (CSO)/silver nanoparticle (AgNPs) composite was designed and prepared via a self-assembly process with rGO through a microwave assisted method. The material, isolated as a nano-crystalline graphenic material, was characterized by ATR-FTIR and UV-Vis spectroscopies, X-ray powder diffraction, TEM microscopy, and energy dispersive X-ray spectroscopy. The nano-rGO/CSO/AgNPs composite can be described as a biopolymer in which AgNPs have been anchored on the surface of CSO-functionalized graphitic rGO sheets.

1. Introduction

Mesoporous networks in graphene oxide (GO) composite structures are particularly appropriate for the formation of nanoparticles in comparison with traditional routes [1, 7]. On the other hand, chitosan (CS), a well-known compound resulting from chitin N-deacetylation, shows functional amine segments (carboxyl, hydroxyl, epoxy, and $-NH_2$ groups) in the molecular skeleton that can form nanostructures with GO or reduced graphene oxide (rGO) via interactions such as hydrogen bonding. Morphological characterization of rGO/GO-CS composites have demonstrated the formation of porous 3-D nanostructures which feature a high adsorption capacity.

By contrast, silver nanoparticles (AgNPs) are prone to form aggregates on GO via electrostatic interaction [8] and are susceptible to be enveloped by chitosan, CS [9]. Thus, the integration of aforementioned materials in a one nanomaterial can be deemed as an achievable goal. In fact, GO/CS/AgNPs and rGO/CS/AgNPs ternary nanocomposite systems have been designed so that anchoring of AgNPs to CS functionalized graphitic GO/rGO sheets can occur [8, 10].

The present study is focused on investigating the preparation of rGO/CSO/AgNPs nanocomposites (were CSO stands for chitosan oligomers) through a microwave-assisted method, which has not been reported before to the best of the authors' knowledge. Microwave chemistry involves a dipolar mechanism and ionic conduction [11, 12].

Successful synthesis of AgNPs by microwave-assisted methods has been reported in the literature [13, 14] and is well-known as a rapid process for the preparation of metallic nanoparticles (e.g., gold, platinum or palladium) [15]. The homogeneous heating of the reaction medium when microwave irradiation is used improves the reaction rate to hasten the fast nucleation and crystal growth of nanoparticles, yielding monodispersed nanoparticles with high crystallinity and small and uniform size distribution [12, 13]. Moreover, microwave-assisted synthesis has lower energy consumption requirements in comparison to conventional heating methods [13, 16]. This emerging synthesis technique has already proved to be a valuable alternative to selectively prepare materials and nanomaterials, in almost quantitative yields and with greater precision than using conventional heating [17, 18].

2. Experimental Section

2.1. Materials and methods

High quality reduced graphene oxide (rGO), produced from helical-ribbon carbon nanofibres by chemical methods, was supplied by Grupo Antolín Ingeniería (GRAnPH Nanotech, Burgos, Spain). The sample consists of few layer (up to five) graphene oxide nanoplatelets, highly crystalline and with a large cross section (above 10 square microns) [19].

Medium molar mass chitosan (CAS No. 9012-76-4) was purchased from Hangzhou Simit Chemical Technology Co. Ltd. (Hangzhou, China). Silver nitrate (CAS No. 7761-88-8) was supplied by Merck Millipore (Darmstadt, Germany).

The formation and assembly of rGO/CSO/AgNPs was carried out in a Milestone Ethos-One microwave. An ultrasonic machine, model CSA 20-S500, 20kHz was used for the sonication of the solutions.

Infrared spectra were recorded with a Thermo Nicolet 380 FT-IR apparatus, equipped with Smart Orbit Diamond ATR system, in order to identify the chemical functional groups. Optical absorption spectra in the UV-Vis region were recorded with a Shimazdu UV-2450 UV-Vis spectro photometer. X-ray powder diffractograms of the samples were obtained using a Bruker D8 Advance Bragg-Brentano diffractometer, in reflection geometry. Transmission electron microscope (TEM) micrographs were collected with a JEOL JEM-FS2200 HRP equipped with an Oxford instruments INCA Energy TEM 250 EDS probe.

2.2. Preparation

2.2.1. Chitosan oligomers preparation

An aqueous solution of chitosan oligomers (CSO) was prepared from chitosan with average molecular weight (140000-300000g/mol) in 2% AcOH at pH 4-6 with the addition of 0.3M H_2O_2, under constant agitation for 12 hours. Subsequently, it was subjected to 6 intermittent periods of sonication, of 5 minutes each, keeping the temperature below 60ºC. The molecular weight of the resulting oligomer was about 2000g/mol, in accordance with the tests reported by Sun et al. [20].

2.2.2. Silver NPs preparation

Silver nanoparticles were prepared by a sonication method, without resourcing to UV stabilization (used, for example, in [21]), as follows: an aqueous solution of $AgNO_3$ (50mM) was treated with sodium citrate (30mM) and the resulting solution was cooled and stirred at a temperature between 5 and 10ºC. Subsequently, it was deoxygenated with an inert gas (N_2) for over 30 minutes and the pH was adjusted between 7 and 8. Polyvinylpyrrolidone was added to prevent the silver nanoparticles aggregation. A 10mM solution of $NaBH_4$ (reducing agent) was then added dropwise: The first droplet made the solution turn from colorless to yellowish and successive droplets led to an intensification of the yellow color (care had to be taken so as to avoid an excess of reducing

agent, which would lead to a brownish color). After vigorous stirring for one hour, the yellowish solution was sonicated for 3-5 minutes and then allowed to rest and stabilize for at least 24 hours in a refrigerator at 5ºC.

2.2.3. Microwave synthesis of the composites

The rGO/CSO/AgNPs composites preparation procedure was as follows: 17mg of reduced graphene oxide were mixed with 2mL of the silver nanoparticles solution (170μg/mL), 100μL of the chitosan oligomers solution (22.7mg/mL) and ethylenglicol (1mL). Water was then added till a volume of 10mL was obtained. A microwave treatment was subsequently conducted at 60ºC or at 120ºC for 10 minutes with stirring (heating ramps of 5 and 10 min, respectively). The obtained products were centrifuged, decanted and washed with ethanol for characterization by analytical techniques.

3. Results

### 3.1. Vibrational characterization

The vibrational spectra of the rGO/CSO/AgNPs composites prepared by microwave treatment at 60ºC and 120ºC are depicted in Figure 1. The two spectra were very similar to each other (only showed small differences in the absorbance intensity), indicating that they corresponded to the same material. Typical peaks such as –NH stretching of CSO, carboxyl C = O and C−O, and alkoxy C−O groups could be readily identified in the spectra, while the peak assigned to epoxy C−O at 1226cm^{-1} had disappeared. In addition, amide peaks could be clearly observed at 1636cm^{-1} and less clearly at 1412cm^{-1}. Thus, according to Jiao et al. [10], the FTIR results demonstrate the presence of rGO and the successful synthesis of Ag nanoparticle-containing rGO-based composite materials.
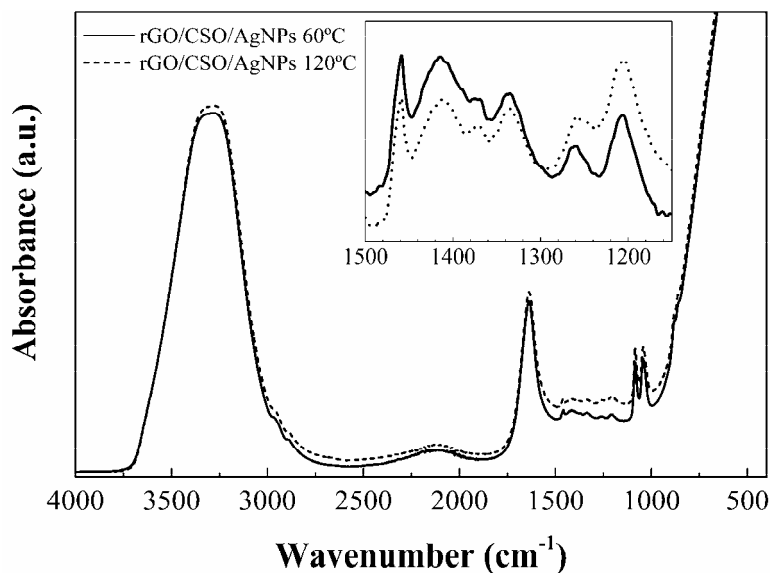
Figure 1. ATR-FTIR spectra of the rGO/CSO/AgNPs composite material.

3.2. Optical absorption

To get an insight into the dynamics of the formation and assembly of rGO/CSO/AgNPs, intermediate UV-Vis absorption spectra at different reaction stages were collected (see Figure 2). Whereas the spectrum of rGO revealed an absorption peak centered at 230nm and a shoulder peak at about 300nm [22, 23], a new peak appeared at about 430nm, associated to AgNPs decorated onto the rGO/CSO, which implies the formation of rGO/CSO/AgNPs. It is also worthnoting that the material obtained at 120°C showed higher absorbance than that obtained at 60°C.
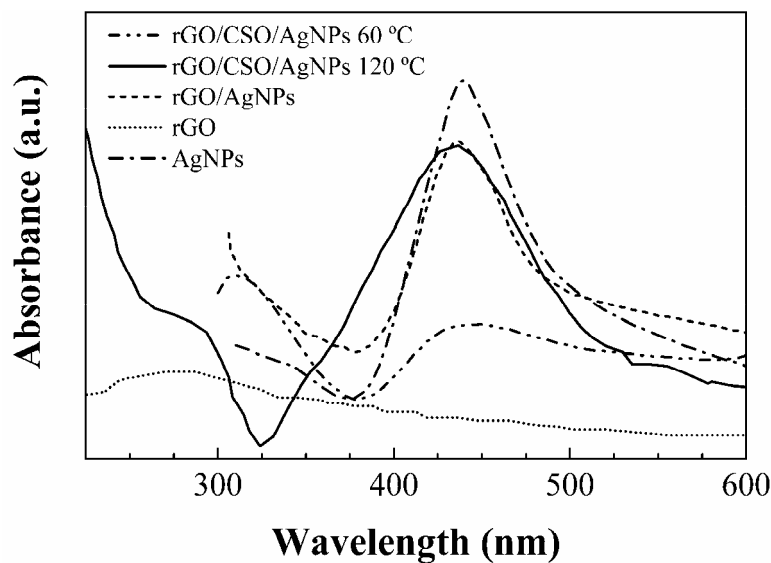
Figure 2. Visible absorption spectra for rGO/CSO/AgNPs composite and its intermediate products.

3.3. X-ray powder diffraction

The XRD pattern of the composite (Figure 3) exhibited a main peak at $2\theta \approx 22^\circ$ (which, after deconvolution, corresponded to two peaks at $d = 4.44\text{Å}$ and $d = 3.70\text{Å}$) followed by a minor peak at 38° ($d = 2.36\text{Å}$). These peaks indicates the presence of the three components of the nano-composite: the peaks at 21° and 24° are to be assigned to CSO and rGO, respectively, in very good agreement with those reported by Matei et al. [24] and Park et al. [25], while the peak at 38° is assigned to AgNPs according to JCPDS patterns [26].
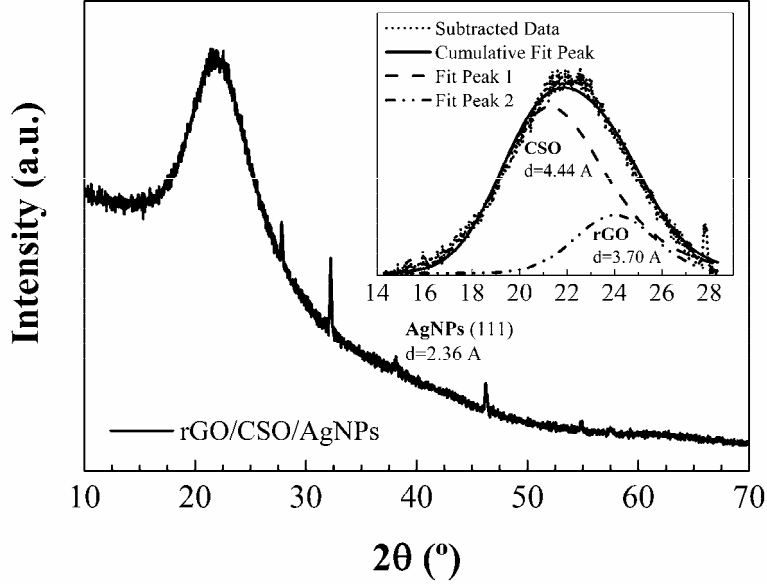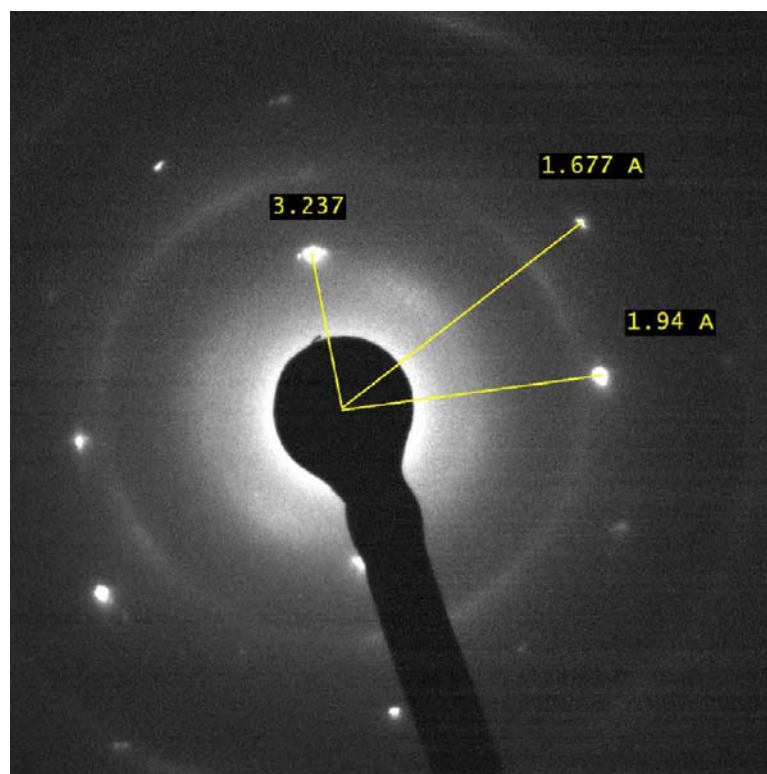
Figure 3. XRD pattern of nano-rGO/CSO/AgNPs composite showing CSO, rGO, and AgNPs peaks.

3.4. Imaging of Debye-Scherrer rings

On the basis of d-spacing from Debye-Scherrer rings (Figure 4), three assignations could be made: 1.94Å to (200) reflection of AgNPs; 1.677Å to graphite (004) reflections; and 3.237Å to planar stacking of graphene sheets.

Figure 4. Debye-Scherrer rings of nano-rGO/CSO/AgNPs composite.

3.5. Textural properties and EDS analysis

TEM images of a well-dispersed and stabilized sample of the synthesized composite are shown in Figure 5. It could be observed that spherical silver nanoparticles with a diameter ranging from 10 to 30nm (Figure 6) were embedded in a matrix of CSO functionalized graphitic rGO sheets and also that no particles were observed outside this matrix.
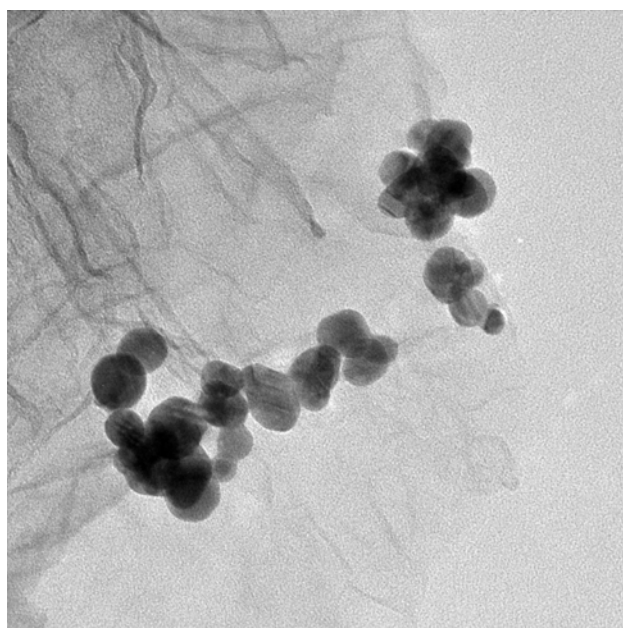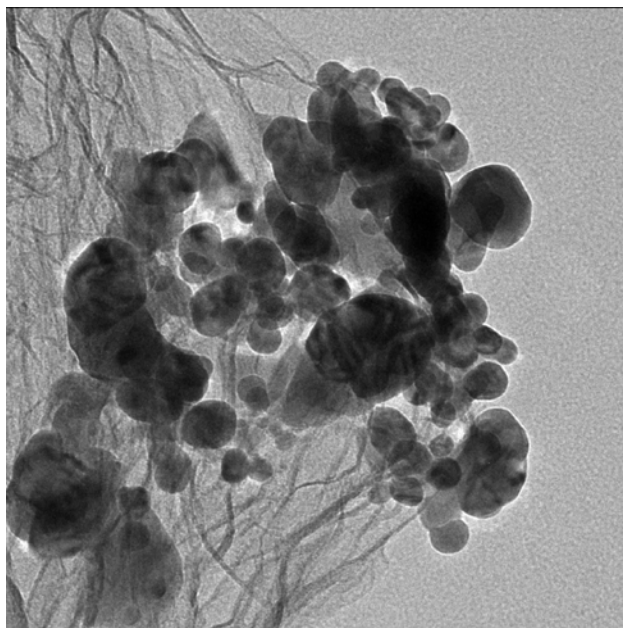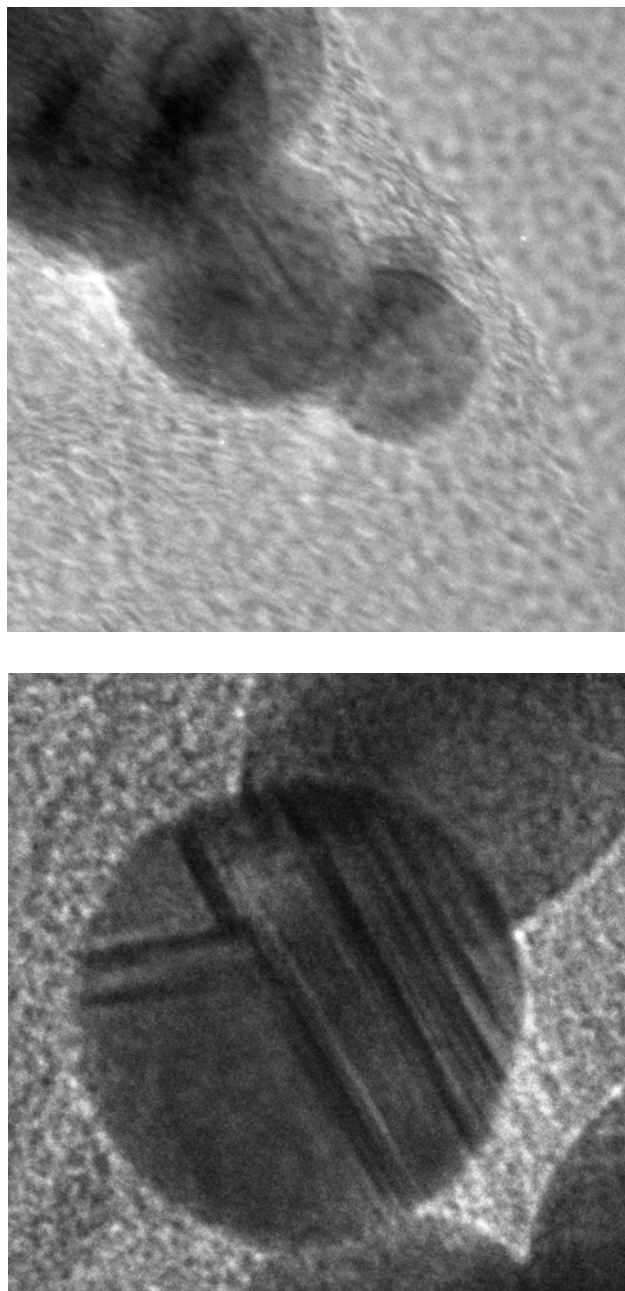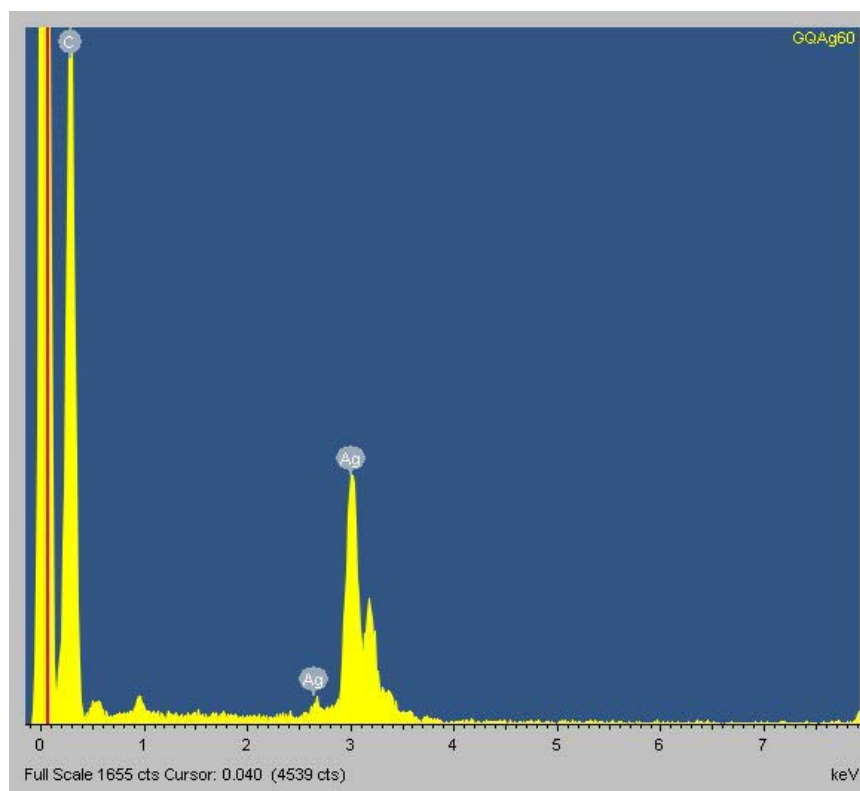
Figure 5. TEM photographs showing the spherical Ag nanoparticles on the CSO functionalized graphitic rGO sheets.
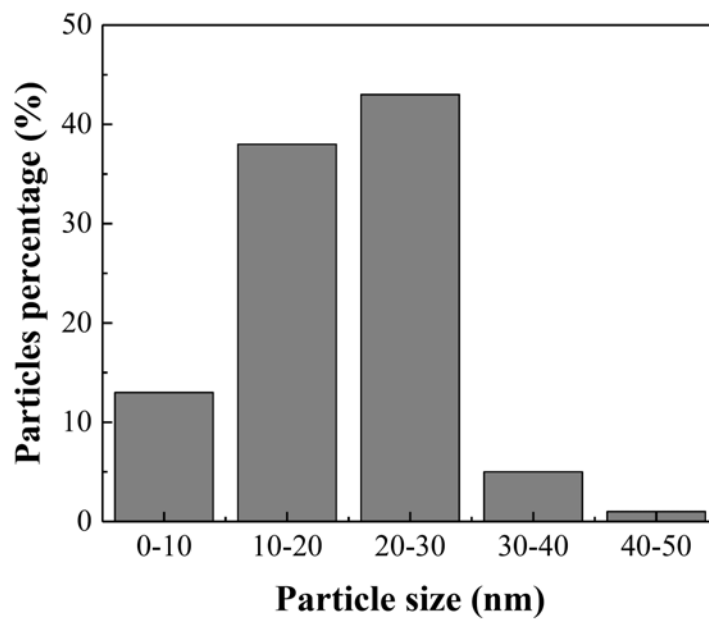
Figure 6. Particle size distribution for AgNPs.

EDS analysis (Figure 7) further confirmed the claim of the presence of AgNPs in the composite.

Figure 7. EDS scan showing the presence of C and Ag elements.

4. Discussion

The nano-composite reported in this paper has different characteristics from those of similar composites prepared from GO and rGO with chitosan and silver nanoparticles [8, 10]. The main feature of the composite discussed herein is to be a crystalline solid of graphenic texture and not a hydrogel [10]. This difference must be referred to the low proportion of chitosan in our nanocomposite (11.6%) and to the fact that the chitosan is in the form of oligomers, instead of in the form of high or medium molecular weight chitosan. Another important difference is determined by the very low presence of nanosilver in our composite (2%), in contrast to the very high percentages used by other authors, reaching proportions of 88% in weight [8].

Regarding the operating conditions followed in the microwave reactor for synthesizing nanocomposite variants, the results indicate that it is sufficient to apply a program with a temperature as low as 60ºC (for 10 minutes, with stirring) to obtain the desired material. The differences in morphology, properties and yield versus the material obtained at 120ºC cannot be deemed as significant.

5. Conclusion

The facile design and synthesis of a rGO/CSO/AgNPs composite material assisted by microwave radiation has been reported. The CS molecule was chosen due to its functional amine segments in the molecular skeleton that can form porous nanostructures via electrostatic interactions and by hydrogen bonding. Morphological characterizations of the obtained composites show the formation of silver nanoaggregates on CSO functionalized rGO sheets by a self-assembly process. The *in situ* formed silver nanoparticles appeared uniformly anchored on rGO sheets. The use of microwave in the preparation of the reported nanohybrids provides a novel method for the development of new multifunctional nanocomposites on the basis of the existing nanomaterials.

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