March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

Synthesize rGO-AG NPs by Pulse Laser Ablation in Less Pulse Energy and Ablation Time

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Abstract:
The rGO-Ag NPs have been synthesized successfully by pulse laser ablation PLA as a considered to be environmentally friendly and free of residues from chemical reactions. The high purity silver plate (99.9%) was immersed in the prepared graphene oxide solution and irradiated with the Nd-YAG laser at wavelength 1064 nm, energy 160 mJ, repetition rate 6 Hz , 10 ns pulse width and (200,300,400,500,600) pulses (ablation time) , to obtain silver nanoparticles anchored on the reduced graphene oxide sheets forming the nanocomposite rGO-Ag NPs. The nanocomposite rGO-Ag NPs were analysis by UV-Visible spectroscopy, (FTIR) Fourier Transform Infrared spectroscopy, X-ray diffraction (XRD), (AFM) Atomic force microscopy and (SEM) scanning electron microscope. The results have shown the graphene oxide has a reduction as confirmed by UV-VIS, XRD and FTIR and the AFM, SEM studies confirmed the presence of silver particles in nanoscale and anchored on the reduced graphene oxide sheets.
Keywords:

I. INTRODUCTION

Recently, numerus methods have been modified to synthesize of graphene or its derivatives with inorganic nanoparticles (NPs), particularly noble metal [1] to have nanocomposites applied in many fields.

Therefore, graphene oxide (GO) nanosheets decorated with Ag NPs have been interesting for their larger surface area and high electrical conductivity it made it a candidate for many applications [2] [3]. Hence, rGO-Ag NPs nanocomposites have been synthesized by several methods, including Ag mirror reaction [4] [5], ultrasonic irradiation [6] [7], solution-based single-step method [8] [9], microwave irradiation [10] and electrostatic force directed assembly [11]. These methods are not eco-friendly, involving multi-steps and require strong reducing agents.

On the other hand, the pulsed laser ablation in liquid (PLAL) it has many advantages such as simplicity, cleanness, and easy synthesis particle in nanoscale. Behand the targets and laser parameters, the liquid media, which gives tight restriction of the removed species, plays key roles in final products by utilizing surfactants as capping agents to avoid the agglomeration of nanoparticles and inorganic salts as reactants to nanostructures [12]. If the liquid media has very small particles (e.g., graphene oxide sheets), it may be totally different and can be expected exceptional structures. Herein, Ag NPs and graphene oxide (GO) are selected as model materials to prove the possibility of the strategy, by using laser ablation of a silver target immerse in an aqueous solution containing graphene oxide sheets.

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

In this study, we propose a novel way to decoration graphene oxide with silver nanoparticles based on pulsed laser ablation in liquid (PLAL) with less pulse laser energy and short ablation time.

II. EXPERIMENT

1- Preparation of graphene oxide (GO)

Preparation of GO follows a previous report [1]. In this study the final concentration of GO was 0.6 mg/l in distilled water was sonicated for 1 hour until a homogeneous yellow dispersion was obtained.

2- Prepare the rGO-AgNPs Nanocomposite

2-1 Preparation of Ag plate

Amount of silver powder (5g) (99.99% purity; Sigma Aldrich, St. Louis, MO) was compressed with hydraulic piston after cleaning with ethanol, under pressure 22 MP with diameter 2 cm and thickness (2 mm), then it was placed in the oven for one hour at 500°C, for annealing. A silver plate was polished using a polished paper, to remove the impurities and then washed with ethanol and distilled water.

2-2 Syntheses of rGO-Ag NPs by laser ablation in liquid

The previous silver plate prepared were immersed in 2 mm below the liquid surface on a bracket in a glass vessel filled with 5 mL of the GO solution. Then, the silver plate was exposed by (200,300,400,500,600) pulses by using with a pulsed Q-Switched Nd: YAG laser. The pulse duration of 10 ns and 6 Hz repetition rate at wavelength 1064 nm with an energy of 160 mJ per pulse as shown in figure 1. The solution was stirred continuously during ablation.

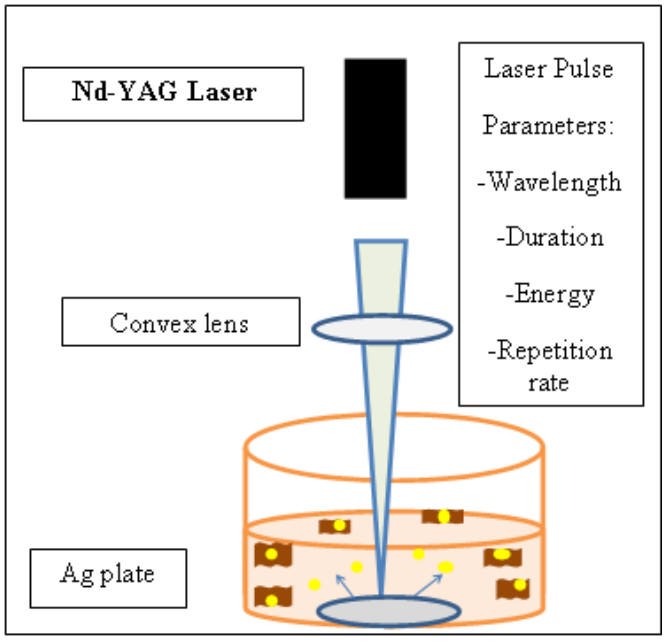


Figure 1. schematic illustrated that Ag NPs decorated on GO sheets at room temperature. The Ag NPs are tightly bonded to each GO sheet's surface, forming a hierarchical micro/nanostructure.

The samples were rename as:

1-S_1 at 200 pulses

2-S_2 at 300 pulses

3-S_3 at 400 pulses

4-S_4 at 500 pulses

5-S_5 at 600 pulses

The optical studied have done by using a UV-Visible spectrum for the colloid directly and for

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

XRD, AFM and SEM analyses were prepared by dropped the suspension on pieces of silicon wafer and then drying them in the oven at 50 ° C for 10 min.

III. RESULTS AND DISCUSSION

Figure 2 depicted the UV-visible spectrum. As results, the absorption peaks for GO is characterized by the presence of a prominent single peak at 229 nm due to the π- π* transition C=C bonds, whereas rGO-Ag nanocomposite exhibits two peaks, one at 245 nm and another at 408 nm.

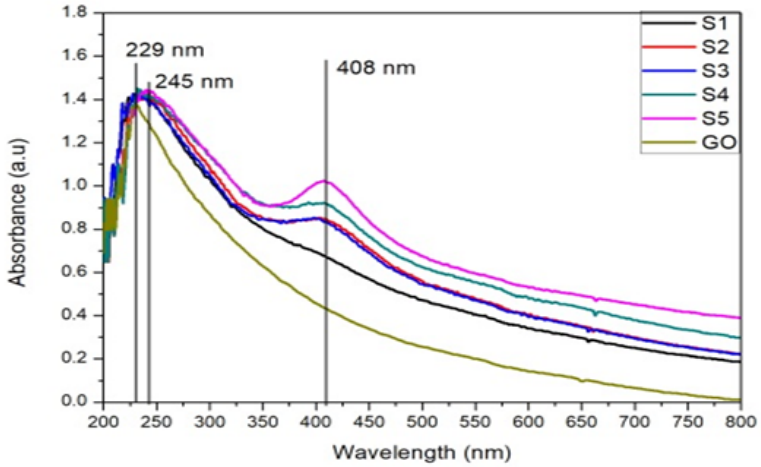


Figure 2. show the Uv-vis absorption for GO, S1, S2, S3, S4 and S5, respectively.

The first peak of GO but have a red shift 16 nm is observed which is assigned to restoration of charge conjugation [1] in GO sheet. The simultaneous appearances of peaks due to both GO and Ag in the absorption spectra is a clear indication of the formation of rGO-Ag nanocomposite [1]. Also, we can recognized a broadening at the half maximum like shoulder approximately at 300 nm is mainly due to the n-π* (C=O) transition represented a partial reduction for GO. AgNPs was indicated by the localized surface plasmon resonance LSPR peak of AgNPs at around 400 nm. In all the cases, formation of AgNPs is evident from this LSPR peak. For Ag NPs grown in GO suspension, with increasing ablation time or pulses number, the intensity of LSPR peak absorbance marginally increased but this increase is not linear at the increase in the all samples. Here, for pulses from 200-300 pulse the increasing in number of pules given increase in the intensity of absorption, while noted there are no effect in the efficiency of ablation when the number of pulses from 300-400 pulse and then see a remarkable increase in absorption at 500 and 600 pulse. We can explain this by self-absorption process because many silver nanoparticles are generated and GO nanosheets on the path of the incidental laser light. On the other hand, with increasing number of pules (500-600), the intensity of LSPR peak absorbance marginally increased.

The study the morphology of nanocomposite using SEM as in figures (3).

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

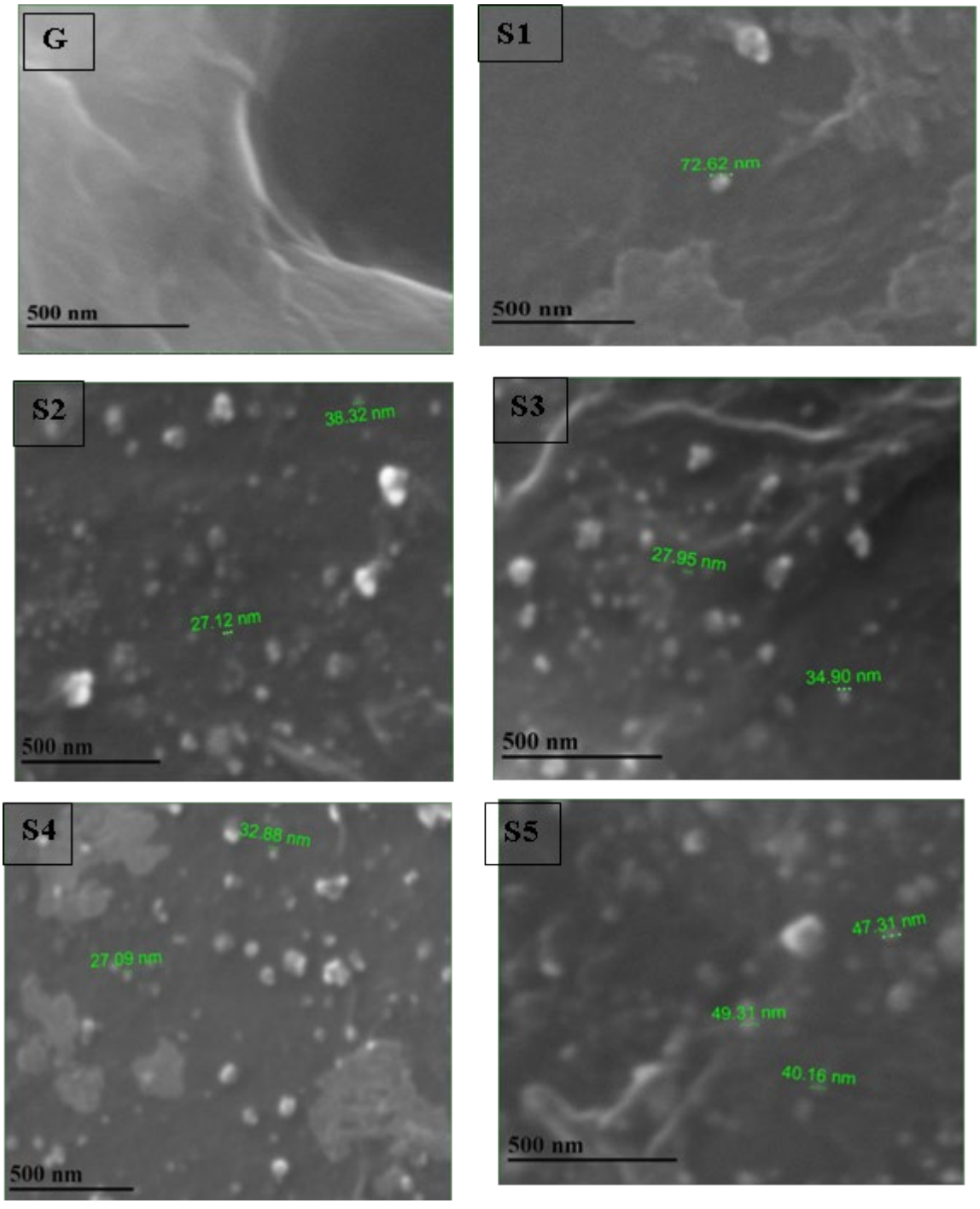


Figure 3. SEM for GO and S1, S1, S2, S3, S4, S5 respectively.

We can see the homogeneously distribution of Ag NPs on the GO sheets increasing with increasing the number of pules comparison with the image of GO, the size of silver nanoparticles approximately same for 300,400,500 and big different for 200 and for 600 the biggest nanoparticles near 50 nm. Moreover, all the Ag NPs spherical for all samples and also the aggregation for the particles absent for all samples.

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

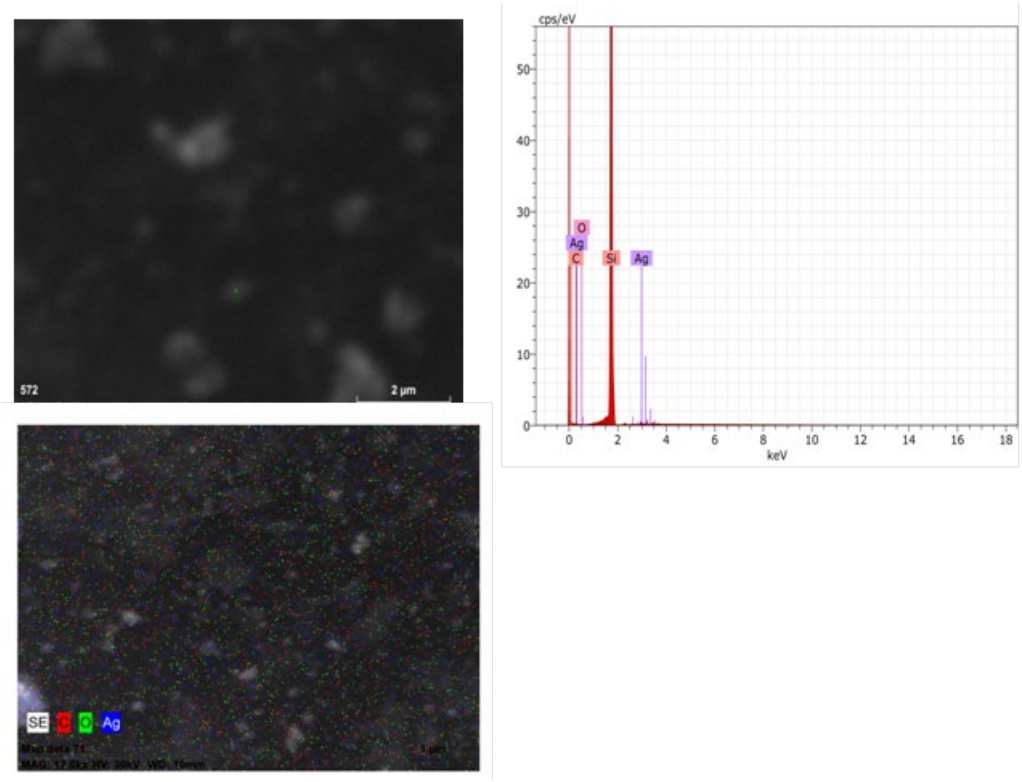


Figure 4. (A) EDX spectrum and (B) X-ray mapping images for the sample S5.

Figure 4 (A) shows the Energy dispersive X-ray analysis (EDX spectrum) of sample S5. The results illustration the presence of C, O, and Ag in the sample, which further demonstrated the successful formation of reduced graphene oxide/Ag nanocomposite as in table 1.

Moreover, the related element mapping are applied to verify the distribution of elements in rGO-Ag NPs. Four types of elements (C, O, Ag and Si) are recognized, as shown in Figure 4 (B), are confirmed to disperse homogeneously in the selected area of rGO-Ag NPs and the Si come from silicon wafer that using as subtract.

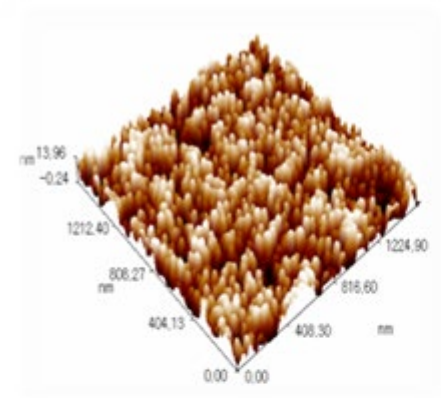
Table (1) show the atomic and weight percentage for the sample rGO/Ag NPs nanocomposite.

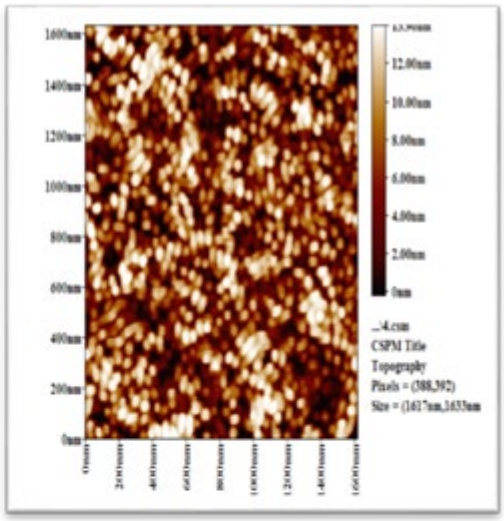
element	At %	Wt %
Si	82.18	89.90
C	17.36	8.12
Ag	0.31	1.30
O	0.15	0.68
total	**100.00**	**100.00**

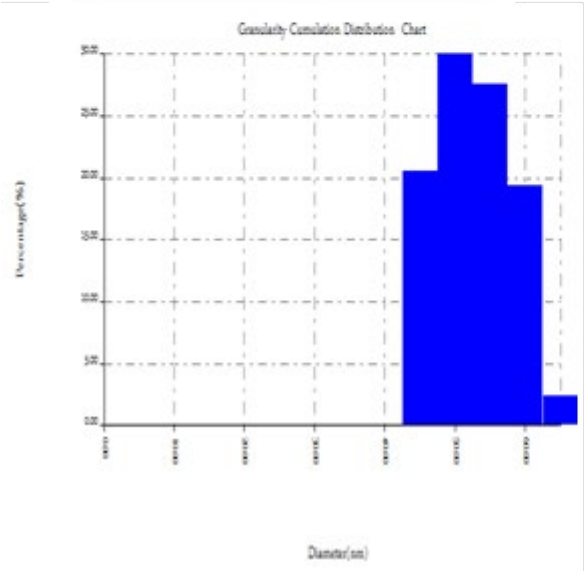
Interestingly, in rGO superposed with Ag nanoparticles and reduced, Ag crystals are deposited on reduced graphene oxide surfaces as spacers between adjacent sheets. Hence, it could provide a large surface area for the attachment of Ag NPs.

The AFM images of the five samples structures in 1D, 2D and statistical distribution showed in the figure 5, can also be observed as a clear increase in particle size with an increase in the number of pulses, while the energy was constant, as shown in table (2).

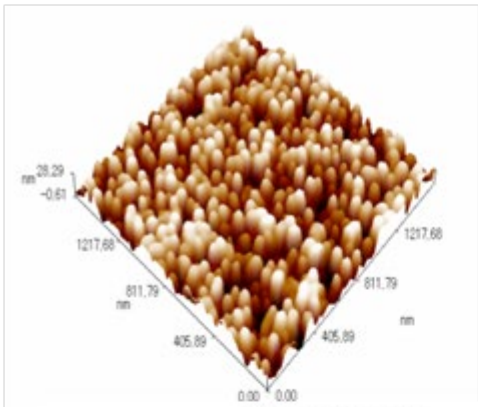
March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

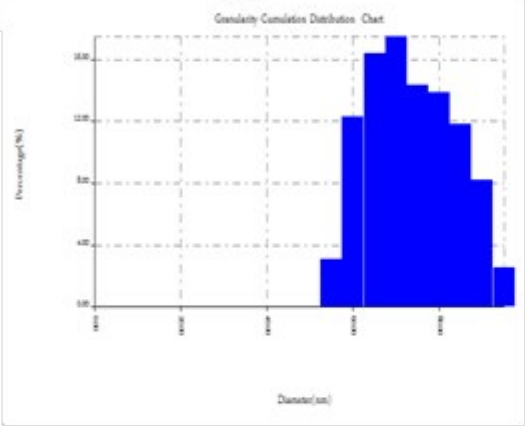


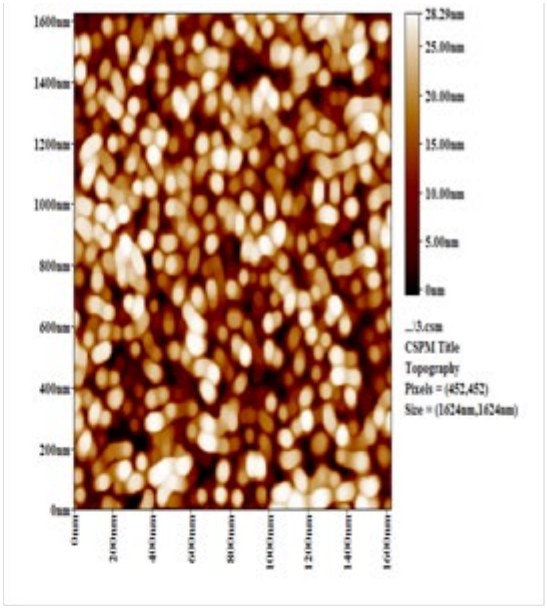


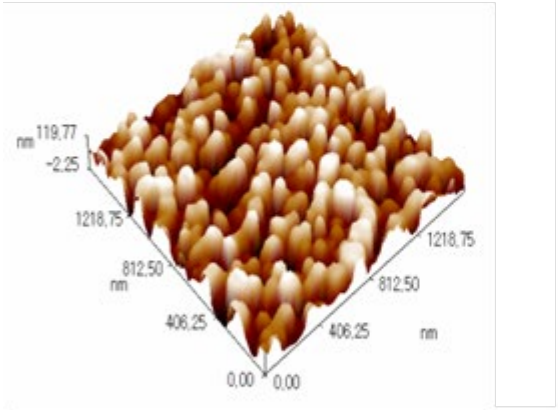


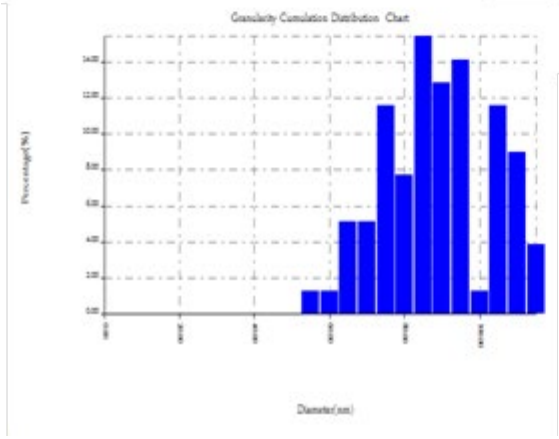
March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

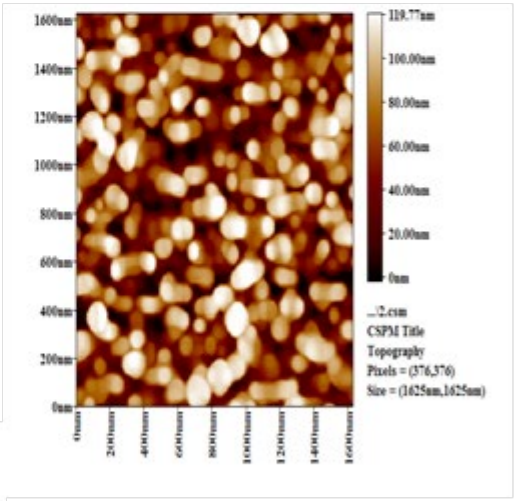












March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

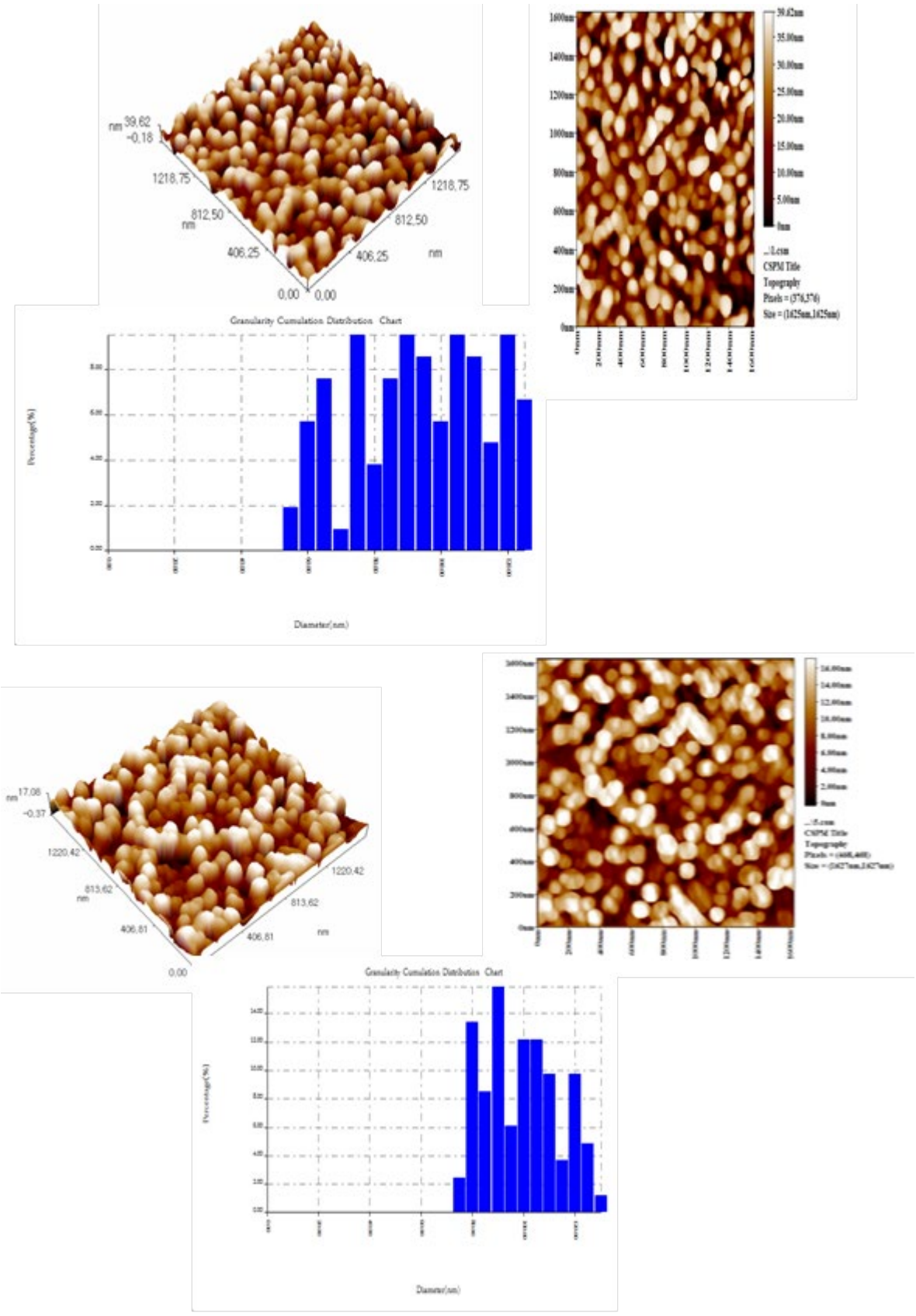


Figure 5. shows AFM images of the five samples structures in 1D, 2D and statistical distribution.

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

Table (2) explains the relationship between particle size and number of pulses.

Samples	No. of Pulses E160 mJ	Avg. Diameter nm))
1	200	50.23
2	300	71.39
3	400	86.06
4	500	91.54
5	600	96.69

The FTIR spectroscopy for the samples GO,S1,S2,S3,S4 and S5 in figures 6,7,8,9,10 and 11 , respectively show more information about the rGO-Ag nanocomposites.

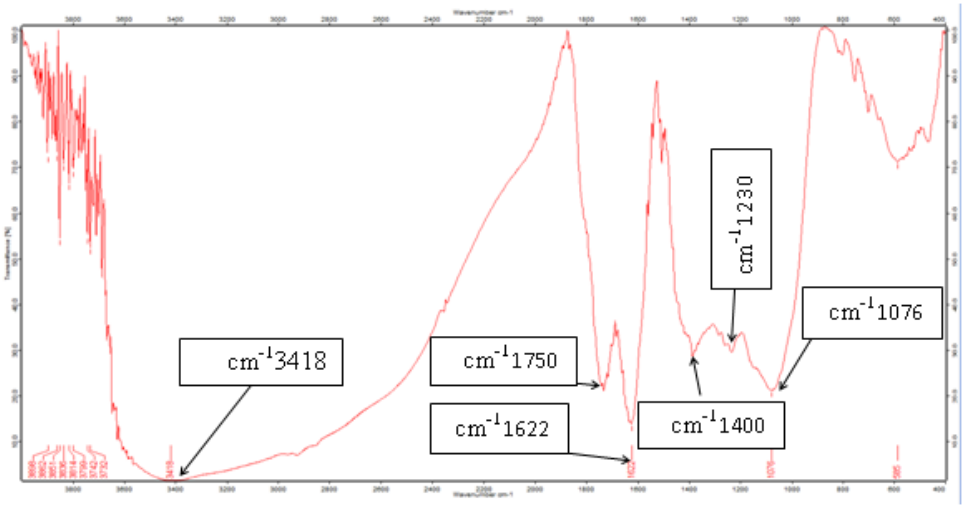


Figure 6. Transmission FTIR spectra of GO

The FTIR spectrum of GO as shown in Figure (4) the presence of C=O in carboxylic acid and carbonyl moieties~ (1770 cm^{-1}), C=C bonds (1622 cm^{-1}), C-OH of carboxylic groups ~ (1400 cm^{-1}), C-O-C bonds (1230 cm^{-1}) and C-O of epoxy or alkoxy groups (1076 cm^{-1}).

The peak of O-H stretching vibrations in (3418 cm^{-1}) are attributed to the hydroxyl and carboxyl groups of GO and remaining water between GO sheets. These hydrophilic oxygen-containing functional groups provide GO sheets with a good dispensability in water, these results are consistent with the researcher's findings [1].

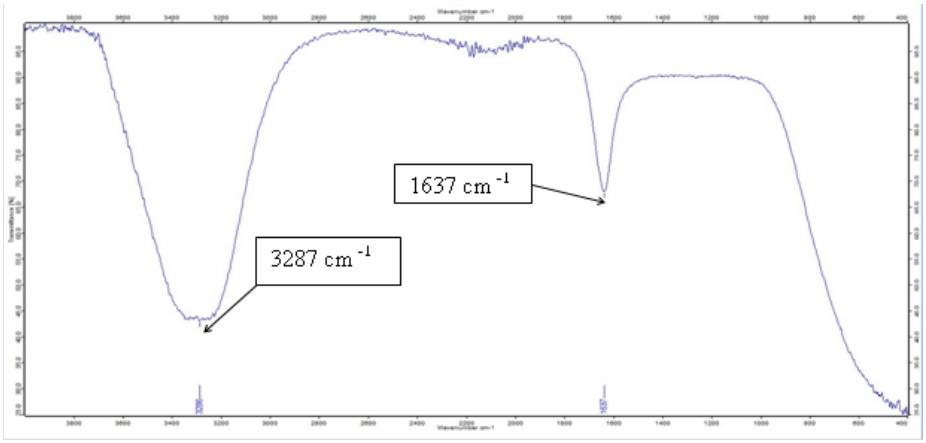


Figure 7. Transmission FTIR spectra of rGO-Ag (S1)

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

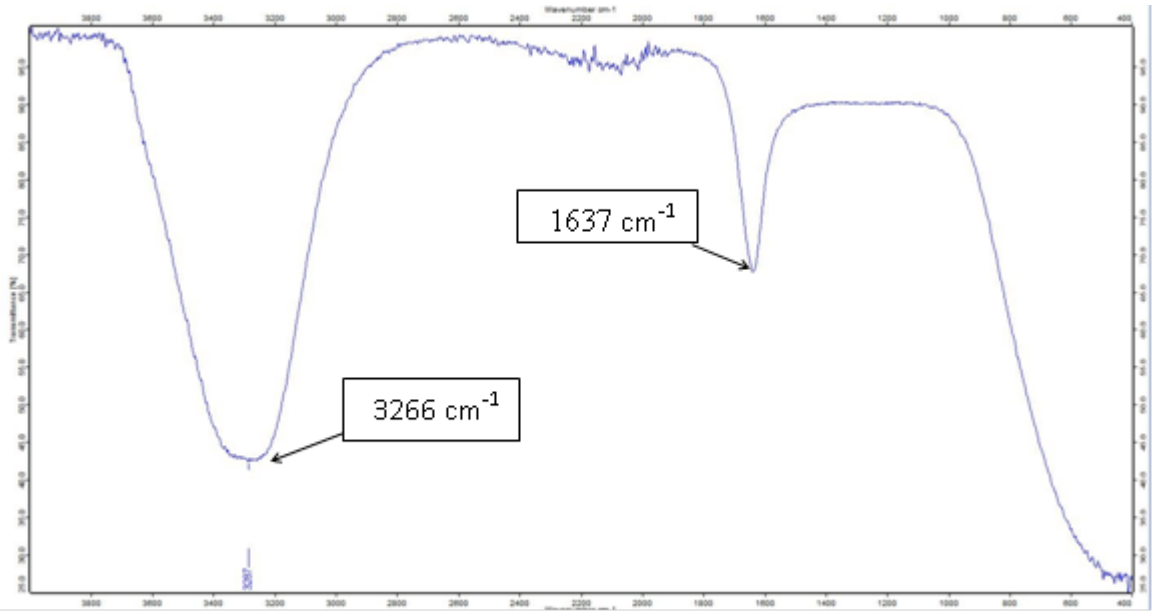


Figure 8. Transmission FTIR spectra of rGO-Ag S2

FTIR spectrum for rGO-Ag shows a decrease in intensity of the oxygen-related functional groups especially C=O and O−H groups and also arising the peak belonging to the group C=C at the expense of the decrease of the group C=O to the extent of vanishing, at 1622 cm−1, (skeletal C=C vibration in rGO sheets) which reveals the reduction of graphene oxide.

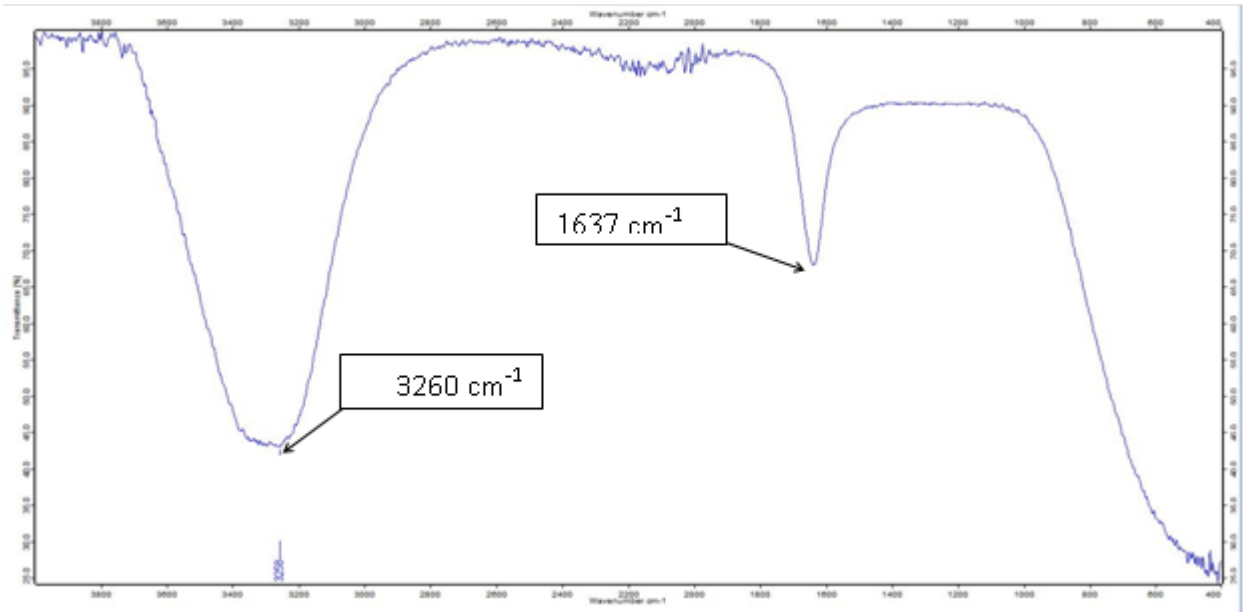


Figure 9. Transmission FTIR spectra of rGO-Ag S3

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

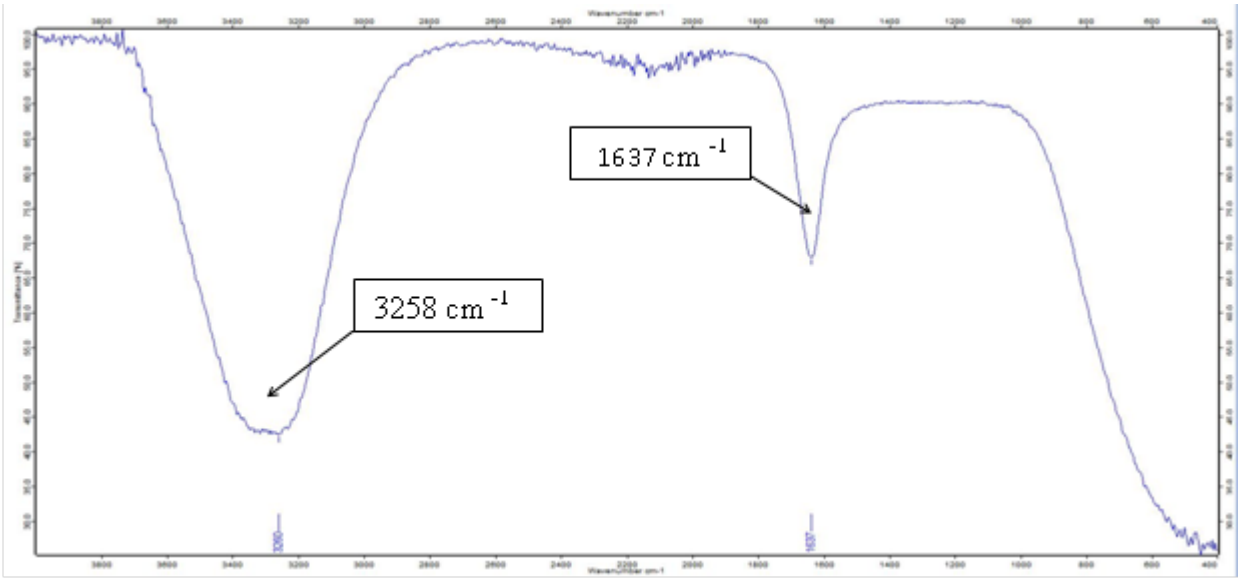


Figure 10. Transmission FTIR spectra of rGO-Ag S4

Additionally, there is a decrease in the intensity of the absorption bands at approximately 3260 cm−1 for the rGO-Ag NPs samples figure 9.

The all major absorption peaks relate to the O-H stretching vibrations, centered at 3418 cm-1 for GO and (3287 cm-1 for S1, 3258 cm-1 for S2, 3260 cm-1 for S3, 3266 cm-1 for S4 and 3258 cm-1 for S5) in the rGO-Ag NPs nanocomposites [13]. Moreover, the decrease of the O-H stretching absorption intensity and the shift in wavenumber in the nanocomposites is attributing to interactions between the silver ions and hydroxyl groups of GO. [13].

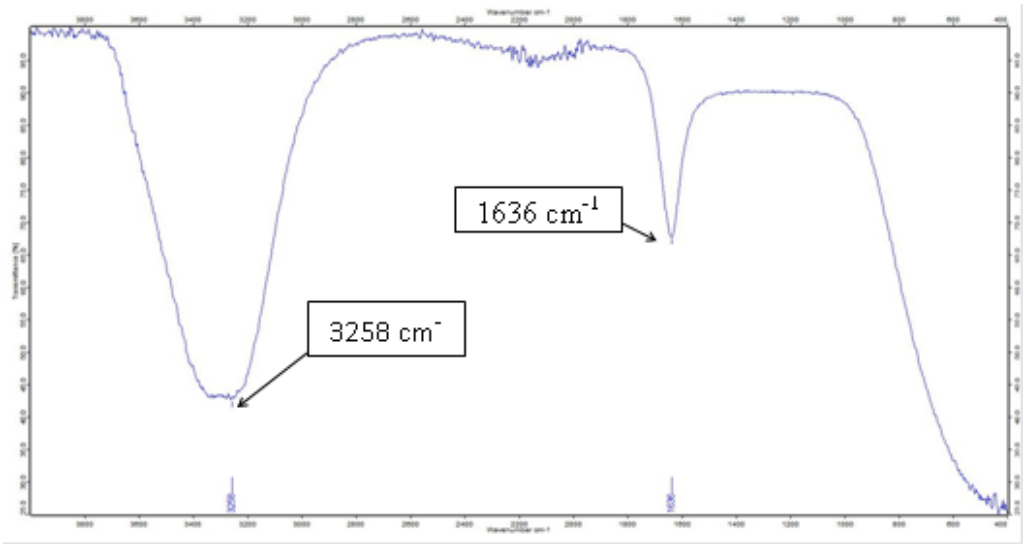


Figure 11. Transmission FTIR spectra of rGO-Ag S5

These results are consistent with the researcher's findings, but in a different way of preparation [1, 13].

The crystalline characterizes of bulk material and all prepared materials were analyzed by XRD measurements. Figure 12, shows the XRD pattern of silver plate.

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

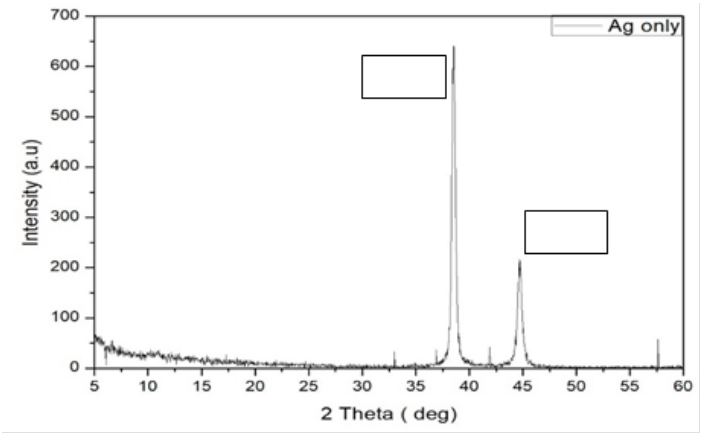


Figure 12. XRD pattern of Ag plate

The peaks observed at 2θ in 38° and 45°are attributed, respectively, to the crystalline planes (111) and (200) due to the face-centered cubic (FCC) structure of silver nanoparticles.

While the figure 13 shows the X-ray diffraction of GO and the five samples of the rGO-Ag NPs after pulse laser ablation.

In the figure 13 , there are four main peaks at 2Θ~(10,22,32 and 45)°, whereas 2Θ= (10.31,10.47,10.27,10.56,11.53 and 11.89)° attributed to GO, and the interlayer distance about 0.85 nm was related to the (001) diffraction of GO sheets, while the weak diffraction peak at 2Θ = (28.842, 22.75, 24, 21.9, 20.97 and 20.9) due to rGO attributed to the (002) with d-spacing 0.30 nm of rGO emerged is due to the removal of surface oxygen functional groups from GO surface making the graphene oxide reduced which maybe come from the drying process of GO sample and laser ablation and this can be confirmed by a note the d-spacing value for rGO is much smaller than of GO [3,4].

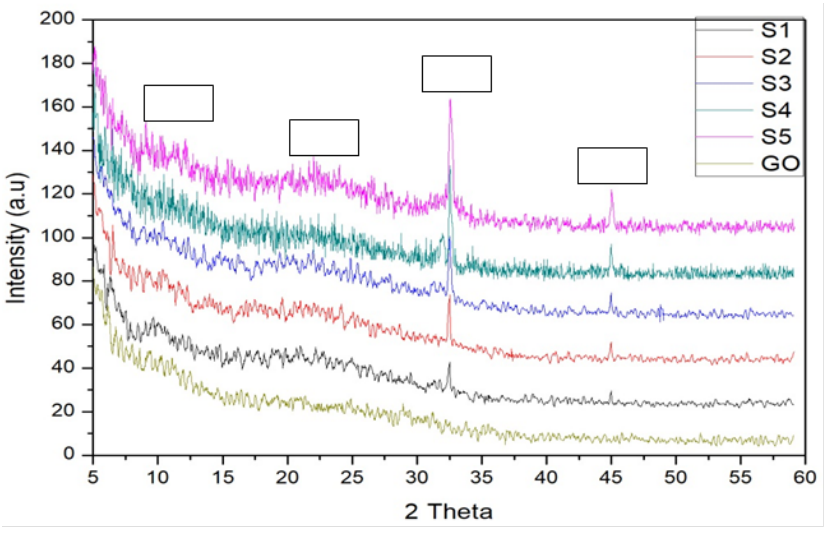


Figure 13. XRD pattern of GO and rGO-Ag NPs for five samples.

Also, noted that the increase in the number of laser pulses increases the intensity of the rGO peak and this indicates the presence of a reduction of the GO and this results corresponds to the UV-vis results. Finally, the last two peaks at 2Θ= (32, 45) ° due to silver nanoparticles.

It is noted that the peak at 2Θ= (38°) for Ag plate in figure (13) was shifted towards to 32° in figure

March-April 2020
ISSN: 0193-4120 Page No. 10946- 10959

(12) because of silver nanoparticles have been affected by the existence of a large amount of oxygen ions found in the composition of GO and water, potentially causing the oxidation of silver. Also, noted that the increasing number of laser pulses cause an increase in the intensity of silver nanoparticles peaks, that means an increased concentration of silver nanoparticles on the graphene sheets.

The crystal size of GO, rGO and Ag nanoparticles are shown in tables 3 are calculated by the Scherrer equation in nanoscale.

Table 3 show the crystal size of GO, rGO and Ag nanoparticles.

	Peak No.	2-theta(deg.)	d(nm)	hkl	FWHM(deg.)	C.S.(nm)
S1	1	10.47	0.84	1	0.167	49.51
	2	22.75	0.39	2	0.245	33.81
	3	32	0.28	111	0.22	37.47
	4	45	0.21	200	o.61	13.06
S2	1	10.27	0.86	1	0.127	63.31
	2	24	0.36	2	0.114	75.35
	3	32.44	0.27	111	0.221	38.51
	4	45	0.2	200	0.54	16.12
S3	1	10.56	0.83	1	0.241	34.66
	2	21.9	0.4	2	0.116	70
	3	32.5	0.27	111	0.212	40.7
	4	45	0.22	200	0.58	14.44
S4	1	11.53	0.76	1	0. 1	86.65
	2	20.97	0.42	2	0.163	51.35
	3	32	0.28	111	0.1	86.65
	4	45	0.23	200	0.55	15.93
S5	1	11.89	0.77	1	0. 1	86.65
	2	20.974	0.41	2	0.163	51.35
	3	32	0.27	111	0.285	28.88
	4	45	0.22	200	0.6	15.4

The crystalline size for GO were (34.66 - 86.65) nm, rGO (33.81 – 75.35) nm and for silver nanoparticles (13.06 – 86.65) nm, shown that all sizes in nanoscale without big difference in the size, this result indicate that the pulse laser ablation in liquid (PLAL) introduced rGO nanosheets decorated with silver nanoparticles in form rGO-Ag NPs nanocomposite.

IV. CONCLUSION

As shown, the pulse laser ablation in liquid (PLAL) successfully producing small silver nanoparticles with a high size distribution on graphene oxide in pure water without any chemical additives, by working with less laser power and small laser beam spot sizes and less time ablation near to 2 minutes. The UV-Vis

spectra of rGO-Ag NPs, show that two main peaks one around 229 nm for GO and second around 410 nm for Ag NPs after the ablation process the first peak shifted to 245 nm indicted that the graphene oxide has reduced. The FESEM indicates that Ag NPs on the reduced graphene oxide sheets are spherical in shape in the range 27-72 nm with high distribution depended on increasing the number of laser pulses.

The FTIR and XRD studies also give the evidence regarding the formation of the nanocomposites, where, FTIR has shown that the graphene oxide has reduced and also the XRD proof that with evidence indicating that the silver nanoparticles have decorated on rGO sheets with small crystalline size.

This study proves that the pulse laser ablation a good tools to decorated metals on graphene sheets and reduced graphene oxide at the same time.

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