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Abstract The PVA-G-Ag nanocomposite have been synthesized effectively by pulsed laser ablation liquid (PLAL) as a considered to be environmentally friendly and free of residues from chemical reactions. The high excellence silver plate (99.99%) and graphite plate (99.99%) was immersed in the polyvinyl alcohol (PVA) solution and irradiated with the Nd-YAG laser at wavelength 1064 nm, power 160 mJ for the silver plate and 80mJ for graphite plate, reiteration rate 6 Hz, 10 ns pulse width and 300 pules for graphite plate and 700 pulse for silver plate. The pure of PVA, PVA-Graphene and PVA-Graphene-Ag nanocomposite were investigated using UV-VIS spectroscopy, FTIR and SEM. The absorption spectra of PVA-Graphene-Ag nanocomposite show the presence of two peaks one 0.4 at 272 and second 0.47 at 403 nm. The optical energy gap (Eg) decreased from 5eV of a pure PVA to 4.6eV of a PVA-G-Ag for indirect allowed transition and therefore, decreased from 4.4eV of a pure PVA to 4.1eV of a PVA-G-Ag for indirect forbidden transition. The transmittance and absorption coefficient have been determined. The SEM images confirmed that homogenous composite without aggregation of the components. The average size of nanoparticles of GNPs and AgNPs for PVA-G and PVA-G-Ag nanocomposite was 130 and 115 nm respectively. The FTIR has demonstrated that the connection between the graphene, silver and polymer network was enough to have stable nanocomposite. This investigation demonstrates that the pulse laser ablation decent instrument to decorated metals on the graphene with the presence of the polymer.

Keywords: graphene, AgNPs, PVA-G-Ag nanocomposite, Laser ablation

1. Introduction

The graphene structure has been one of the remarkable discovery in modern physics over the past 14 years. The graphene has been prepared for the first time by the Geim A. K in 2004 which opened many application [1]. Since that time, there has been a lot of research on this discovery [2]. Because the graphene has been discovered as a result, Geim A. K. and et. al. acquired the Nobel Prize in Physics in 2010 [3-4].

Graphene is define as a monolayer of sp^2-hybridized carbon atoms structured in a honeycomb lattice. The hybridized orbitals form strong -bonds in the plane and un-hybridized p-orbitals overlap with neighboring atoms to form -bond. While the -bond is responsible for the most of the structural integrity of graphene, the -bond determines optical and electronic properties. The interaction of graphene with electromagnetic wave is attractive because of the excellent band structure of graphene and the two-dimensional confinement of electrons [5]. It has other fundamental highlights, comprising of wonderful optical transmittance (97.3%)[6]. Graphene has been prepared in several methods like, chemical vapor deposition CVD [7], micro-mechanical exfoliation [8], epitaxial growth of silicon carbide pyrolysis [9], and reduction of the oxidized graphite [10], graphite intercalation [11] and electrochemical technique [12]. These techniques aren't eco-friendly, including multi-steps and needed strong reducing agents. On the opposite hand, the pulsed laser ablation liquid (PLAL) it's a few benefits like cleanness, simplicity, and easily synthesis particle in nanoscale [13].

In view of low Young's modulus esteem, that a few polymers show can be expanded essentially upon the homogeneous joining of graphene, in this manner making polymer/graphene nanocomposites appealing for a scope of utilizations. Polymer- graphene (reduced graphene oxide) nanocomposites as an important materials form for photonic and optoelectronic devices, like graphene-polyvinyl alcohol (PVA) nanocomposite films were fabricated by different techniques like, solution cast method [14], simple solution method [15], a facial aqueous solution[16], while many efforts have been accomplished, which include graphene and diverse metallic nanoparticles, like gold(Au) [17], silver(Ag) [18] and copper (Cu) [19].

In this paper, we proposition a novel method to fabrication PVA-G-Ag nanocomposite by the pulsed laser ablation in liquid (PLAL) with the less pulse laser energy and short ablation time.

2. Experiment

٢.1 Preparation of graphite (G) plate

The measure of graphite powder (5g) (99.99% quality; Interchimiques SA, France) it was a compressed with a hydraulic piston after cleaning the cylinder with ethanol, under pressure 20 MPa with width 2 cm and thickness (2 mm), after that it was annealing for 4 hours at 450°C, for strengthening. A graphite plate was cleaned utilizing a cleaned paper, to evacuate the debasements and afterward washed with ethanol and refined water.

2.2 Preparation of silver (Ag) plate

The measure of silver powder (5g) (99.99% quality; Sigma Aldrich, St. Louis, MO) was pressured with a hydraulic piston after cleaning the cylinder with ethanol, under pressure 22 MPa with width 2 cm and thickness (2 mm), after that it was annealing for one hour at 500°C, for strengthening. A silver plate was cleaned utilizing a cleaned paper, to evacuate the debasements and afterward washed with ethanol and refined water.

2.3 Preparation of solvent of Poly (vinyl alcohol) (PVA)

0.5 g of Polyvinyl alcohol that (molecular weight 18000 g/mol, temperature of glass 75^{o} C and density 1.18g/cm^{3}) has been solvent in 30 ml of deionized water with magnetic stirrer and temperature 50^{o} C for 30 minute.

2.4 Syntheses of PVA-G-Ag nanocomposite by laser ablation in liquid

The prepared graphite plate was immersed in 2 mm under the liquid surface on a bracket in a glass vessel filled with 5 ml of the PVA solution and then, the graphite plate was exposed by (300) pulses using 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 80 mJ per pulse as shown in Figure.1. This colloid solutions PVA-G nanocomposite will redecorate with Ag NPs by immersed Ag target in this nanocomposite solution and exposed by (700) pulses and energy of 160 mJ from the same Q-Switched Nd:YAG laser..

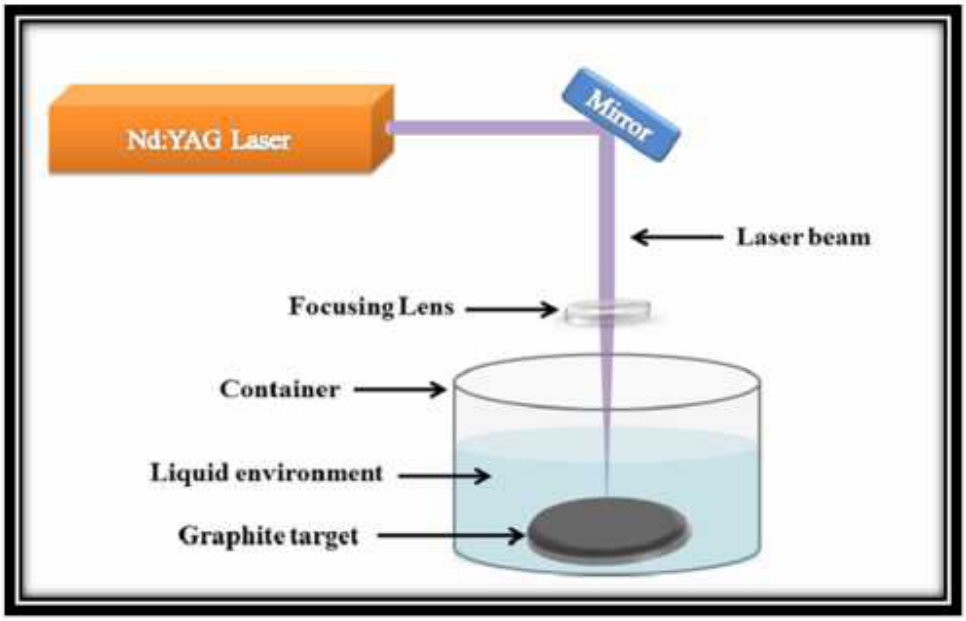


Figure.1 Laser ablation setup

The optical properties have been determined by utilizing a UV-VIS-NIR (UV/1800/Shimadzu spectrophotometer) in the wavelength range of (200-1100) nm for the colloid straight and for the scanning

electron microscope (SEM) and Fourier transform infrared spectroscopy (FTIR) analyses the samples were prepared as a thin film by spin coating method with speed 500 rpm/sec for 20 seconds on a silicon wafer.

3. Result and discussion

The absorption spectra of a pure PVA, PVA-Graphene and PVA-Graphene-Ag nanocomposite are shown in Figure.2. The figure shows that the absorption peak 0.29 at 274nm for the PVA-G nanocomposite due to – * transition of C=C band [20]. These absorption peaks are observed due to Surface Plasmon Resonance (SPR) in the free electron cloud of carbonaceous material electrons [21]. The absorption peak at 274 nm in oxidized graphite is a characteristic feature of graphene [22], while PVA-Graphene-Ag nanocomposite displays two peaks, one 0.4 at 272 nm and another 0.48 at 403 nm. The main peak of graphene (G) has a violet shift 2 nm, this shift of absorption peak toward shorter wavelength (violet shift) indicates the decreased particle size and vice versa [23]. This result agree with the authors [24].

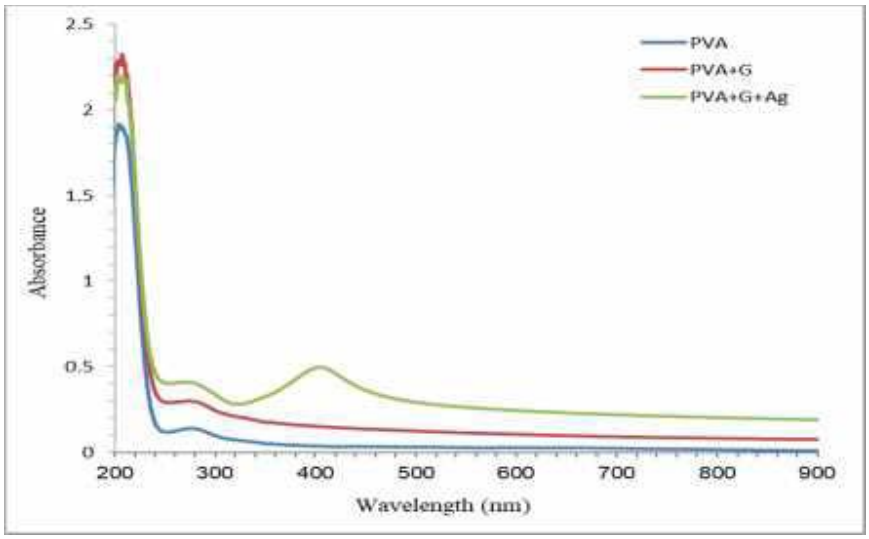


Figure.2 the absorption spectra of a pure PVA, PVA-G and PVA-G-Ag nanocomposite

The optical transmittance of a pure PVA, PVA-Graphene and PVA-Graphene-Ag nanocomposite, has been determined by using the relation (1) [25]:

$$T = 10^{-A} \quad (1)$$

where A: is the absorbance

The transmittance are appeared in Figure 3. The figures show that the transmittance decreased from 98% of a pure PVA to 94% of PVA-G nanocomposite. This decreased was attributed to the presence of the

monolayer graphene, while the transmittance decreased to 88% for the PVA-G-Ag nanocomposite. This influence due to some absorption in that wavelength range (272 and 403nm). This result is agreement with the authors [26].

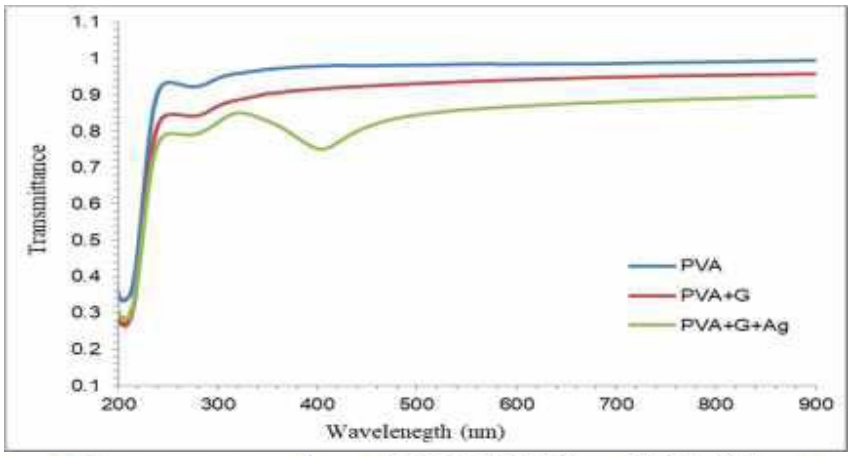


Figure.3 the transmittance spectra of a pure PVA, PVA-G and PVA-G-Ag nanocomposite

To determine the absorption coefficient spectra ( ) for the three samples by using the relation (2) [27]:

$$\propto = 2.303 \frac{A}{t} \qquad (2)$$

Where A: is absorbance and t: is film thickness.

So, Figure.4 show that the absorption coefficient of the three samples. This figure show that the absorption coefficient of PVA-G and PVA-G-Ag nanocomposite increased compared to the pure of PVA. The values of is less than 10^4 cm^{-1}, this indicate that the composites have indirect energy gap [28].

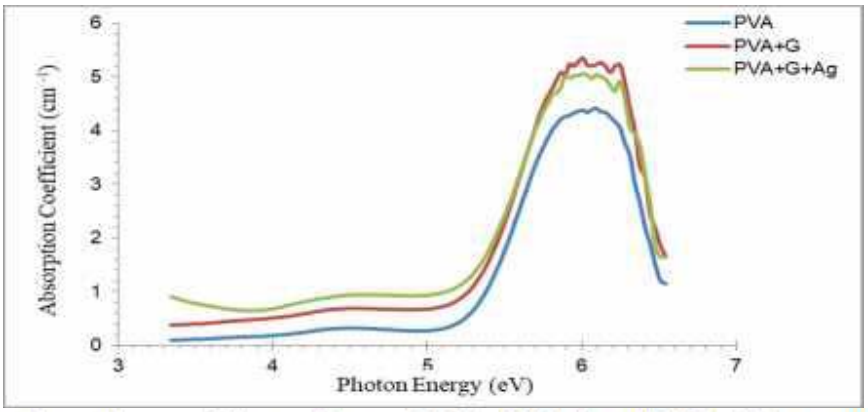
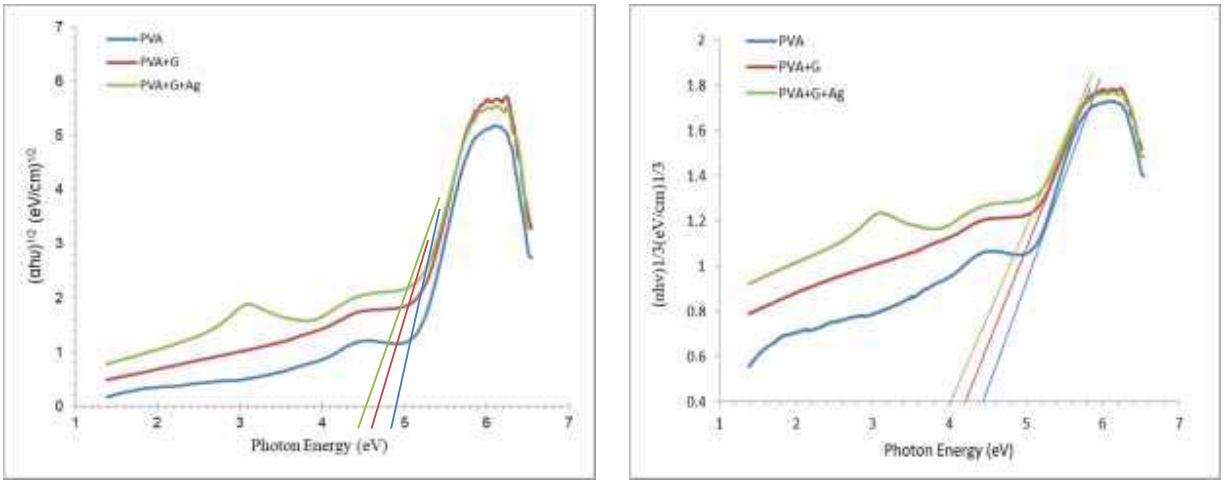


Figure.4 the absorption coefficient of a pure PVA, PVA-G and PVA-G-Ag nanocomposite

By using the following relation (3) to calculated optical energy gap (E_g) [29].

$$=A(h \quad E_g)^r/h \qquad (3)$$

To determine the (E_g) is to scheme a chart between (h)^r and photon energy (h) and find the value of the r which provides the best line diagram are shown in Figure.5. The estimations of optical band hole are chosen by extrapolating the straight pieces of these relations to the h axis and recorded in Table.1. The (E_g)' decreased with the increasing of graphene and graphene-silver respectively. The variety of the determined estimation of the energy hole may reflect the role of graphene and graphene-silver in a variable the electronic structure of the polymeric grid because of the presence of different polaronic and defect levels. Expansion the graphene and graphene-silver substance may bring about the restricted conditions of different shading communities to stretching out in the versatility hole. This association may demonstrate the decline in the energy hole when the including graphene and graphene-silver respectively to the PVA. This result is agreement with the authors [30]



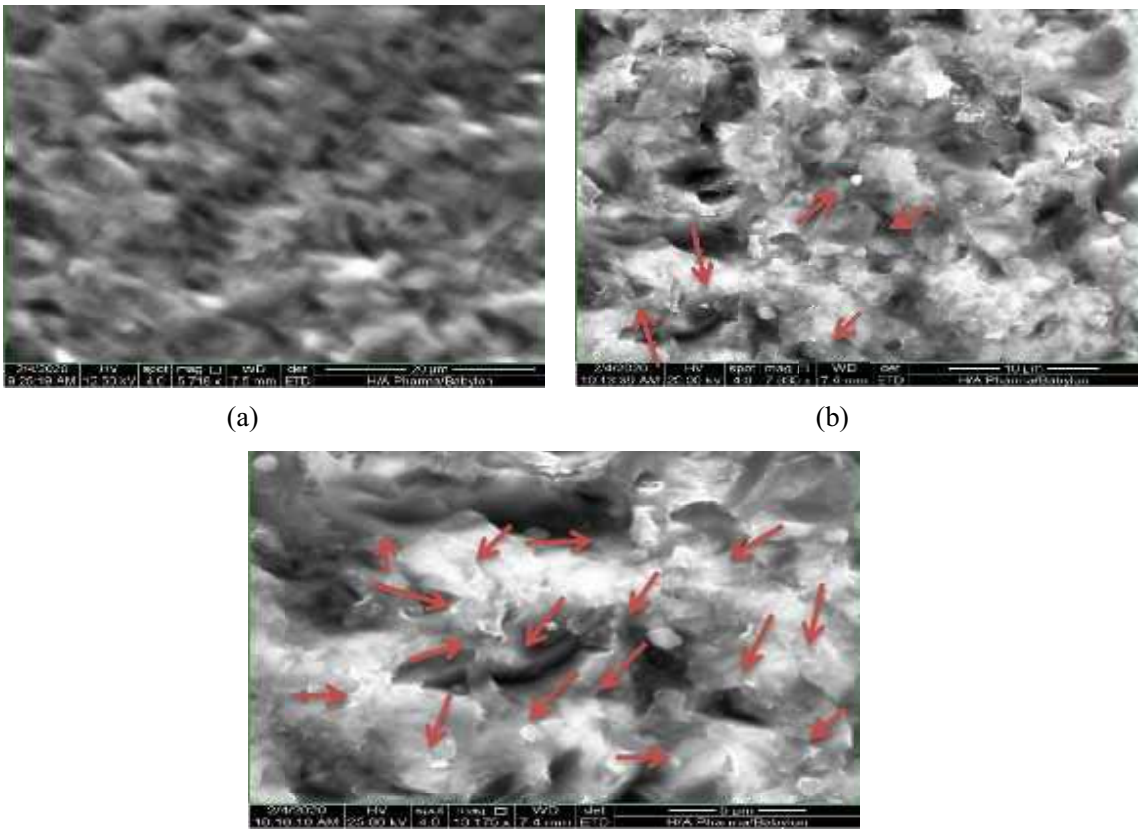
(a) (b)

Figure.5 (a) and (b)The plot of $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^{1/3}$ as a function of photon energy respectively

Table 1. The value of energy gap for a pure PVA, PVA-G and PVA-G-Ag nanocomposite

Component	Allowed E_g(eV)	Forbidden E_g(eV)
Pure PVA	5	4.4
PVA-G	4.8	4.2
PVA-G-Ag	4.7	4.1

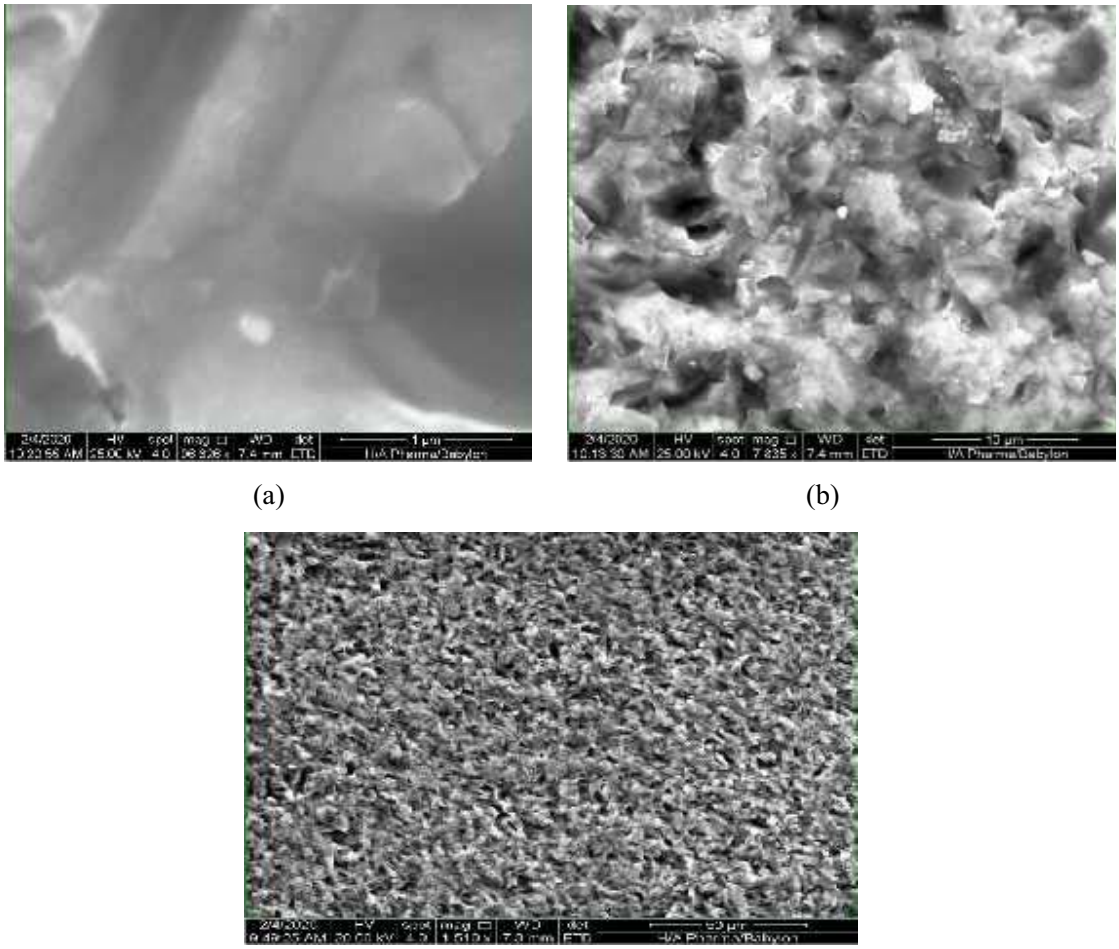
Scanning electron microscopic (SEM) used to show the morphologies for a pure PVA, PVA-Graphene and PVA-Graphene-Ag nanocomposite are appeared in Figure.6. This Figure. a show that the image for a pure PVA was homogenous due to the spin coating method. The SEM images of PVA-G and PVA-G-Ag nanocomposite in Figure. b show that the GNPs are uniformly spread inside the PVA matrix and the average size nanoparticle was 130 nm, while the adding of AgNPs and GNPs to the PVA matrix was apparently noticeable from Figure. c and the average size nanoparticle was 115 nm. From this images of the SEM has been confirmed the incorporation for the PVA-G-Ag nanocomposite that deal with the result of the absorption spectra of this nanocomposite. The microstructural attributes of their materials demonstrated that the G was fairly scattered consistently in the grid even at higher focus because of the solid interfacial communications with the lattice and the turn drying strategy which was utilized during their answer mixing system are appeared in Figure.7



(a) (b)

(c)

Figure.6 (a) (b) and(c) SEM images for (a) pure PVA, (b) PVA-G and PVA-G.Ag nanocomposite



(a) (b)

(c)

Figure.7 (a) (b) and (c) SEM for PVA-G-Ag nanocomposite

Fourier transform infrared (FTIR) spectroscopy was utilized to show data about the compound holding in the recently created nanomaterials. Figure.8 shows FTIR for pure PVA, pure graphite and PVA-G-Ag nanocomposite individually.

In the pure PVA, there are peaks at (3295, 2937, 1713,1240,1140,1086 and 832) cm ^{1} clearly observed, but is missing in the graphite spectra that have only strong peak at 1086 cm-1 has observed and for PVA-G-Ag nanocomposite spectrum, peaks at (3292, 2895,2359,1660,1200 and 1086) cm ^{1} observed without four peaks are missing (1713, 1240, 1140 and 832) cm ^{1}, additionally, the peaks 3295 cm ^{1} and 2937 cm ^{1} had been shifted for lower wavenumber and new peaks at (2359, 1660 and 1200) cm ^{1} has been established.

In all spectrums, the 3295 cm ^{1} and 3292 cm ^{1} due to O–H stretching vibration of carboxyl groups and the absorbed water this absorption peak is shifted to 3292 cm^{-1}[31], a lower wavenumber with the addition of graphene. Meanwhile, the stretching vibration at 2937 cm^{-1} and 2895 cm^{-1} belonging to C–H_2 [32,33]. The vibration at 1660 cm^{-1}, 1200 cm^{-1} and 1086 cm^{-1} are allocated to C=C stretching, and C–O stretching[34,35], respectively with higher intensity in the PVA-G-Ag nanocomposite spectrum than in pure PVA and graphite spectrums, indicating that carbon bond between C, C and O has been established. The above results prove the strong interfacial interaction between graphene and PVA.

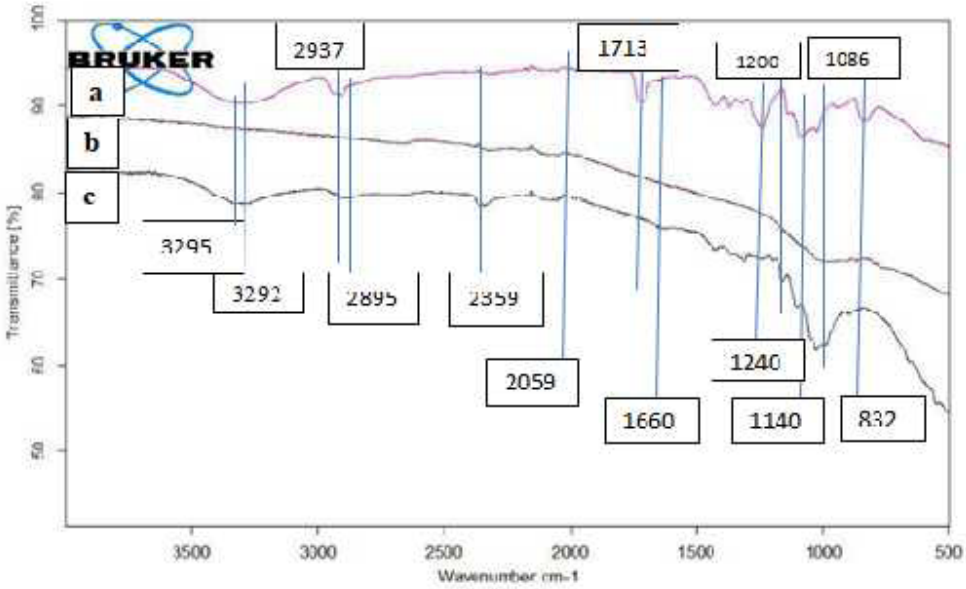


Figure.8 FTIR spectrum for (a) pure PVA, b)pure graphite and (c) PVA-G-Ag nanocomposite respectively

Conclusion

In summary, we have utilized pulsed laser ablation liquid technique to fabricate PVA-G-Ag nanocomposite using with less laser power and small laser beam spot sizes and less time ablation close to 2 minutes. The UV-Vis spectrum of PVA-Graphene-Ag nanocomposite show that two main peaks one 0.4 around 272 nm for G and second 0.48 around 403 nm for AgNPs which indicates that the formation PVA-G-Ag nanocomposite. The energy gap decreased from 5 to 4.6 eV for allowed indirect transition and also decreased from 4.4 to 4.1eV for forbidden indirect transition. The optical parameters such as transmittance and absorption coefficient have been calculated. The SEM images confirmed the homogenous shape without aggregations of prepared samples for pure PVA, PVA-Graphene, and PVA-Graphene-Ag nanocomposite. The FTIR studies also gave the evidence regarding the formation of the nanocomposites, where, FTIR has shown that the interaction between the graphene, silver and polymer matrix. This investigation demonstrates that the pulse laser ablation a good instruments to decorated metals on graphene.

Acknowledgments
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