RESEARCH PAPER

Synthesis of Silver Oxide Nanoparticles (Ag_2O Nps) and Study Their Dispersion into New Polymer Matrix

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ABSTRACT

In this paper, novel polymers were prepared for the first time *via*, which were used as matrices. Silver oxide nanoparticles (Ag_2O- NPs) was synthesized via Eco-friendly route using silver nitrate ($AgNO_3$) as a precursor with sodium hydroxide as precipitation agent in the presence of orange leaves extract as a reduced factor. Silver oxide nanoparticles/ polymer matrixes (Ag_2O-NPs/polymer) were synthesized by solution method. The calcination temperature of silver oxide nanoparticles was 550 °C. The crystal system of Ag_2O- NPs is cubic (a = 1. 892 Å with average size diameter 38.69 nm) was measured by XRD. FT-IR technique was used to confirm the presence of functional groups in Ag_2O-NPs spectrum. The dynamic light scattering (DLS) showed a wider nanoparticle size distribution in two peaks. The morphology analysis were explain by FE-SEM technique, showed a different sizes and spherical shapes nanoparticles with average diameters at 47.45, 57.18 nm and 68.78 nm for Ag_2O-NPs after calcination processes, Ag_2O-NPs/P_1 and Ag-NPs/P_2 matrix respectively. The EDX results presented the elements (Ag=91.2%, O=1.9%).

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INTRODUCTION

Polymers form a very important class of materials without which the life seems very difficult. They are all around us in everyday use; in rubber, in plastic, in resins, and in adhesives and adhesives tapes. The word polymer is derived from Greek words, poly is many and mer is parts or units of high molecular mass each molecule of which consists of a very large number of single structural units joined together in a regular manner [1]. Nanotechnology is a burning field for the researchers. Nanotechnology deals with the Nanoparticles having a size of 1-100 nm in one dimension used significantly concerning medical chemistry, atomic physics, and all other known fields. Nanoparticles are used immensely due to its small size, orientation, physical properties, which are reportedly shown to change the performance of any other material which is in contact with these tiny particles [2]. The silver oxide nanoparticles were synthesized due to their excellent physical and chemical properties [3]. The Ag_2O NPs were aimed to prepare by green synthesis approach using Zephyranthes Rosea flower extract, which includes the low cost, non-toxic by utilizing the extract acts as an excellent reducing and capping agents. The prepared Ag_2O NPs were investigated for structural, functional, morphological, and optical studies [4]. Further, the antibacterial, antioxidant, anti-inflammatory,

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anti-diabetic activities were tested to ensure the bioactivity of Ag2O-NPs [5]. Silver nanoparticles combined with polymers have attracted great consideration because of the widened application goal offered by these hybrid materials. Particularly, silver nanoparticles and polymer composites are promising functional materials in several field such as optical, electrical, and mechanical properties. Many reports in the literature show attempts to synthesize silver nanoparticles-based polymer nanocomposites, with their application in high performance capacitors, conductive inks, and other electronic components Silver nanoparticles have received considerable attention due to their attractive physical and chemical properties and it has been combined with polymers such as polyvinyl alcohol (PVA), poly vinyl pyrrolidone (PVP), poly methyl methacrylate (PMMA) [6,7]. Hence the present study was carried out to synthesize and characterize the silver nanoparticles and Ag-NPs/ polymer composite using eco-friendly method [8].

MATERIALS AND METHODS

Materials

Silver nitrate (THOMAS BAKER, 99%), sodium hydroxide (NaOH) (THOMAS BAKER, 99%) , Ethanol (scharlau, 99%), acrylic acid (CDH, 98%), benzene (CDH 99%), Nitrogen gas (Iraq, 98%), azo bis iso butyronitrile (AIBN) (Germany, 98%) methanol (scharlau, 99%), deoxygenated distilled water and orange leaves.

Preparation of orange leaves extract

The orange leaves were collected from orange trees in Diyala government, then cleaned from suspended dirty by tap water then washed with distilled water dried in shade. They were grinded with electric grinder then sifting then stored away. 30 g of leaves powder was added to 400 mL of deionized water and boiled for 2 hours at 80°C until the solution color change, leaves extract was cool at room temperature and filtered it and stored in refrigerator at 4°C for further studies.

Green synthesis of Ag_2O-NPs using orange leaves extract

Silver nitrate solution was prepared by dissolving (0.5g $AgNO_3$) in the deionized water (50 mL). Plant extract solution was added gradually on the precursor solution under stirring at (40 °C), raise temperature of solution to (90 °C), NaOH (1M) solution was added drop wise to the mixture (salt solution and orange leaves extract) to obtain pH 14 approximately under continuous stirring for (1hour), subsequently the the precipitate was collected and dried in an oven at 80 °C for 2 hours [9,10]. The detailed procedural steps for synthesis of Ag_2O nanoparticles is described in Fig. 1.

Synthesis of polymers

General procedure for the preparation of polymers (p_1 and P_2) are illustrated in Fig. 2. In a 50 mL two-necked round-bottomed flask equipped

$$AgNO_{3(solution)} + \text{plant extract} + NaOH_{(solution)} \longrightarrow AgOH_{(solid)} + HNO_3$$

$$2AgOH_{(solid)} \xrightarrow{550\ °C} Ag_2O\ NPs + H_2O$$

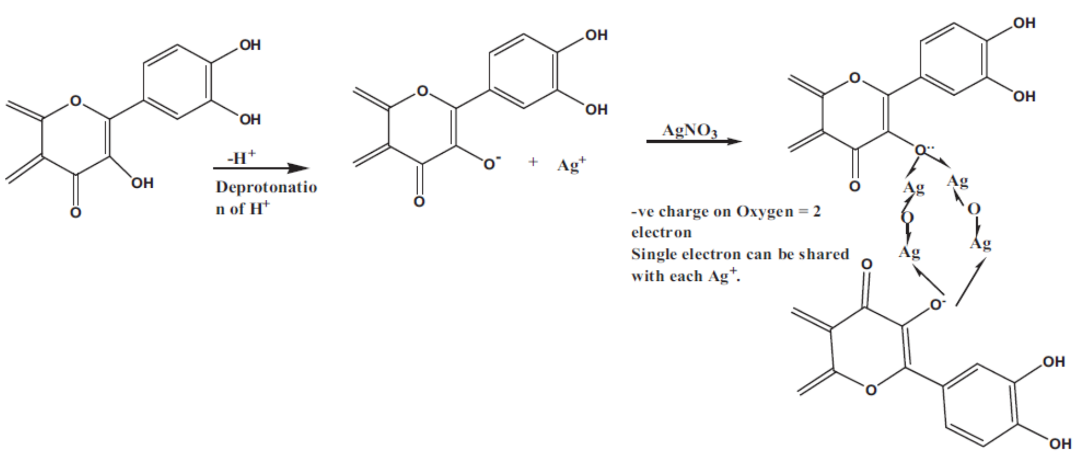

Fig. 1. Reaction Mechanism during the synthesis of Ag_2O NPs [11].

with a reflux condenser, a nitrogen gas inlet tube, and a magnetic stirrer bar, a mixture of solution of compound (B_1, B_2) (0.01 mole) and acrylic acid (0.01 mole ,0.72 g) dissolved in benzene (30mL). AIBN (0.008 mole, 1.3g) was added to the mixture under refluxed for (10 hours), acid was refluxed under a stream of N_2 at 130 °C for 12 h to produce P_1 and P_2, respectively. After cooling the flask to room temperature, the polymer solution was poured into a 25 mL methanol. The formed precipitate was collected by filtration and washed thoroughly with hot water. The polymer was formed and hardened with time [12].

Preparation of Ag_2O-NPs /polymer matrices

Matrices (Ag-NPs/ polymer) were synthesized by dissolving (0.5 g) polymer in THF (20 mL) in beaker (A) and suspended (0.5 g) Ag-NPs in the ethanol (20 mL) in beaker (B) at room temperature. Beakers (A and B) were placed in ultrasonic bath about (30 min) at 50°C. The beaker (A) content was added to beaker (B), the mixture were placed in ultrasonic bath at 70-80 C period (3 hours). The matrices (Ag-NPs/ polymer) as a binary composite [9] were formed after the solvent evaporated [12].

RESULT AND DISCUSSION

Synthesis and Characterization of Polymers

FT-IR analysis

The objective of this study was the preparation of novel polymers (P_1 and P_2) by solution polymerization method from the acrylic acid to using as matrices and stabilizer of silver nanoparticles. The FT-IR spectrum, and 1H and GPC polymers (P_1 and P_2) spectra of are shown in Figs. 3-8, respectively. FT-IR data as shown in Figs. 3, 4 and Table 1.

^{1}H-NMR analysis

^{1}HNMR spectra of the polymers (P_1 and P_2) and

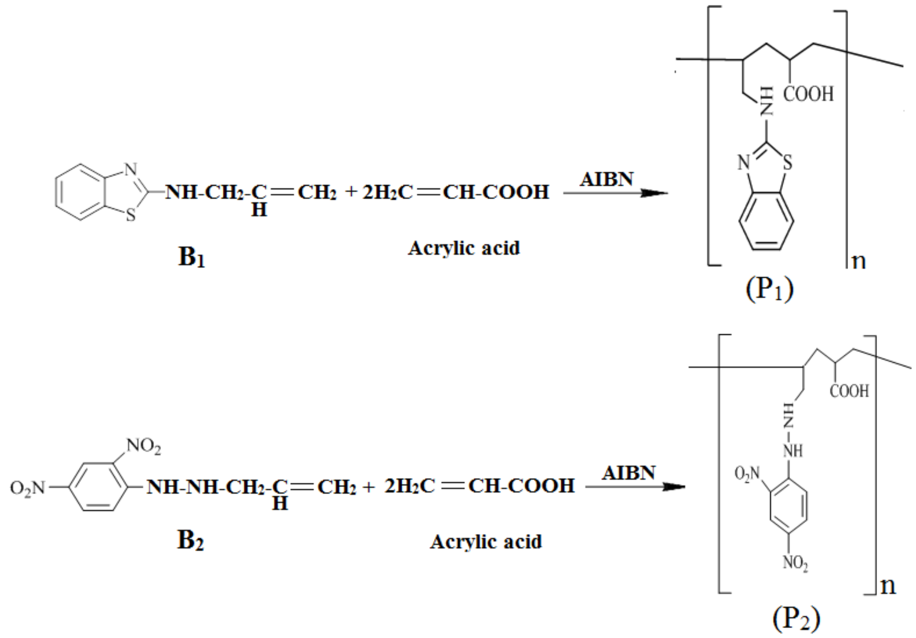

Fig. 2. Synthesis of P_1 and P_2.

Table 1. FT-IR spectrum data of (P_1, P_2).

Polymer	OH	C=N	C=C aromatic	C=O	C-H aliphatic	C-H aromatic	N-H
P_1	3502	1643	1573	1712	2931	3093	3302
P_2	3387	1627	1535	1735	2978	3093	3217

their data were illustrated in Figs. 5, 6 and Table 2, where all the peaks could be readily assigned to the protons. The proton of C-H in the (CH-COOH) group was observed at (1.4 and 1.5) ppm as triplet peak, the proton of C-H attached (CH_2-NH) group show an absorption at (3.27-3.4) ppm as doublet peak. The proton of amine and carboxylic groups were observed at (3.2 and 3.4) ppm and (7.2-7.8 and 7.2-7.8) ppm as singlet and multiple peak, respectively.

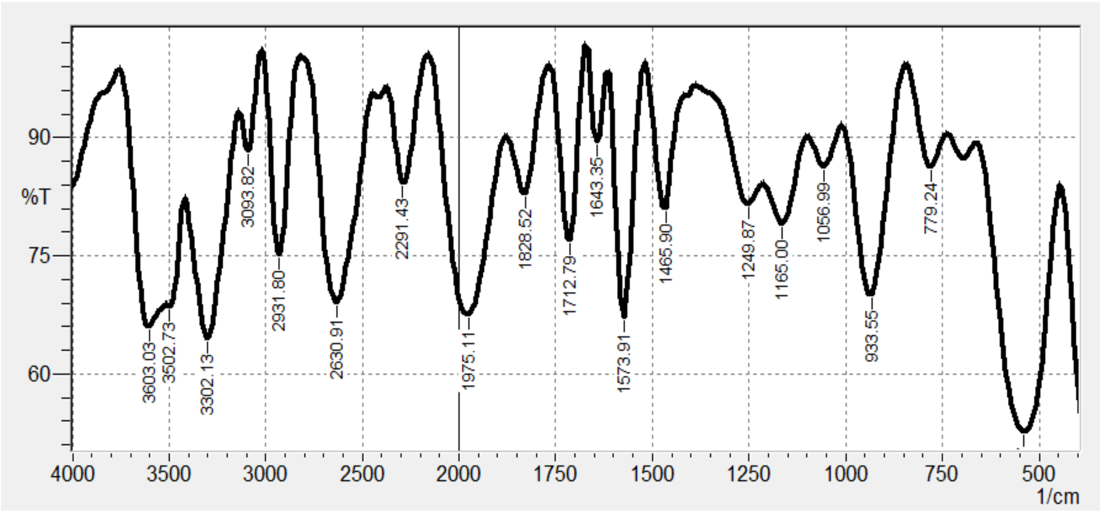

Fig. 3. FTIR spectrum of P_1.

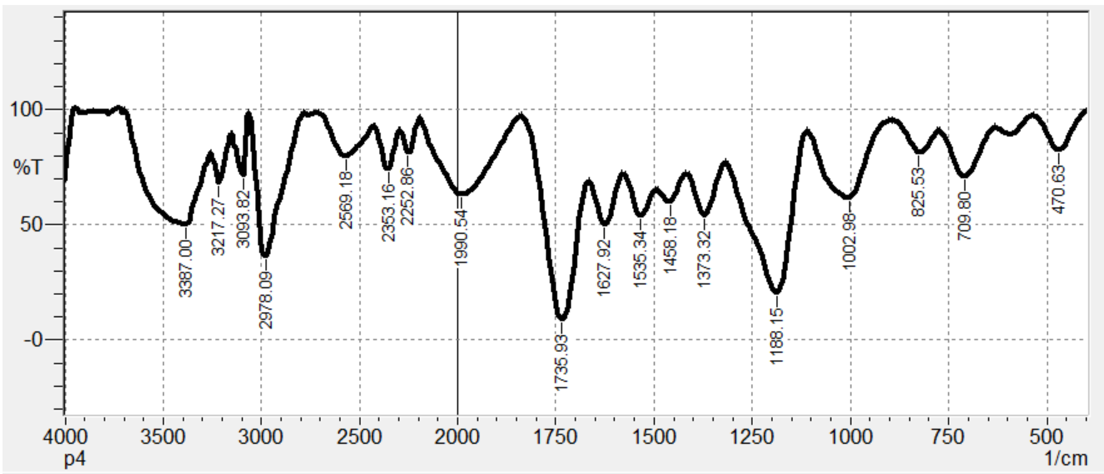

Fig. 4. FTIR spectrum of P_2.

Table 2. [1]H-NMR spectrum for (P_1,P_2).

Polymer	CH_2-NH	CH-COOH	CH-CH_2	N-H	COOH	C-H arom
P1	3.27	1.4	2.3	5.91	12.3	7.2-7.8
P2	3.4	1.5	2.6	4.00	12.3	7.2-7.8

Gel permeation chromatography (GPC) analysis

GPC is a type of size exclusion chromatography (SEC), that separates analyses on the basis of size. Polymers can be chromatography by a variety of definitions for molecular weight including the number average molecular weight (Mn), the weight average molecular weight (Mw) and the size average molecular weight (Mz). Table (3) and Figs. 7 and 8 shown the factors calculate using GPC technique [13] and the GPC chromatogram for the

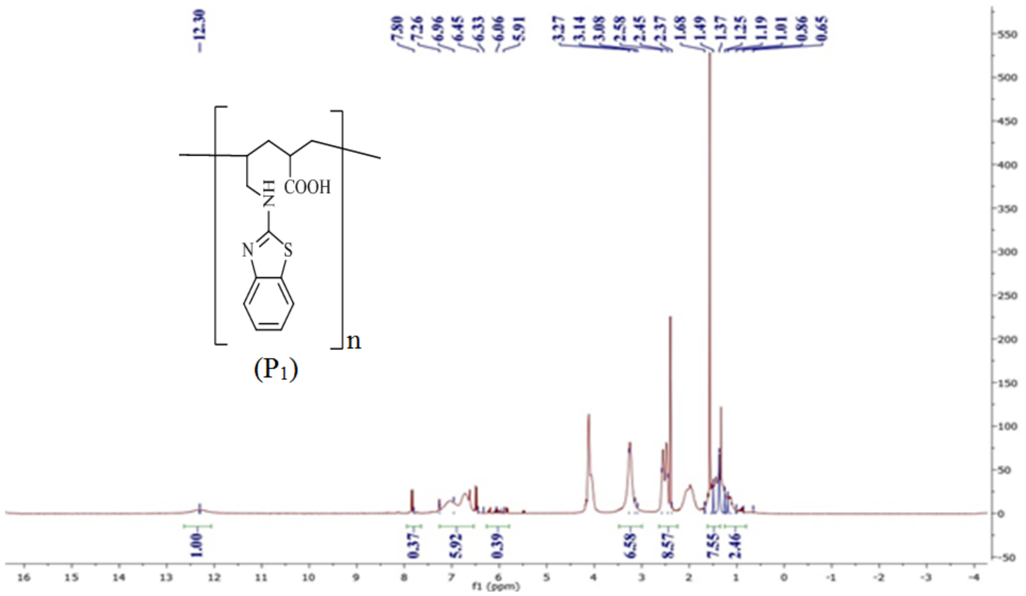

Fig. 5. [1]H-NMR spectrum of P_1.

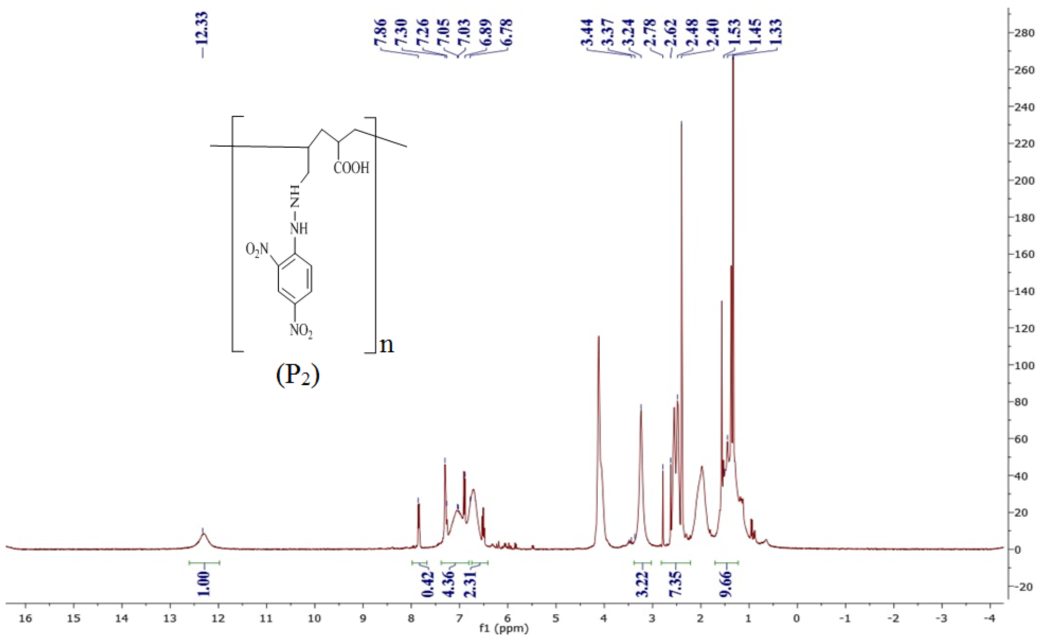

Fig. 6. [1]H-NMR spectrum of P_2.

polymers synthesized.

Characterization of synthesized silver oxide nanoparticles

FT-IR analysis

As shown in Fig. 9, FTIR spectrum (400 to 4000 cm^{-1}) confirms the presence of synthesized silver nanoparticles (Ag_2O- NPs). The broad peak at 3309 cm^{-1} was assigned to the presence of O-H group [14]. The band at 544 cm^{-1}corresponding to Ag–O bond, thus confirming the presence of Ag–O [15]. The absorption at 1457 and 1354 cm^{-1} can be attributed to the symmetrical and asymmetrical bending vibrations of $–CH_3$. The bands at 1623

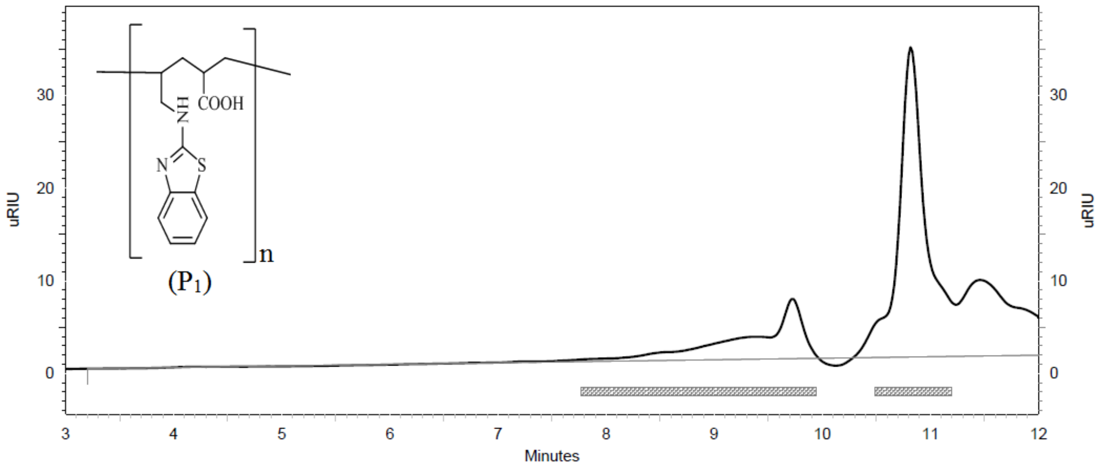

Fig. 7. GPC chromatogram of P_1.

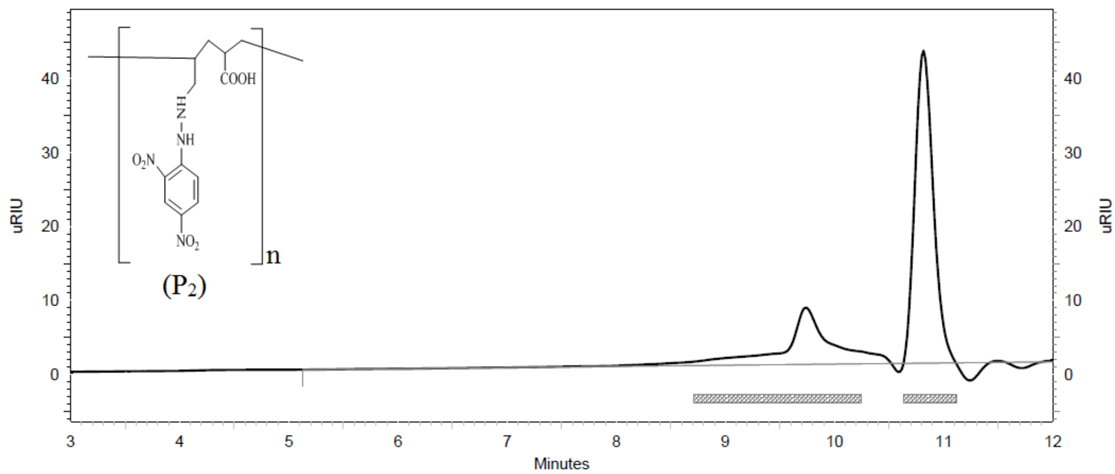

Fig. 8. GPC chromatogram of P_2.

Polymer	M.wt (g/mol)	Mn (g/mol)	Mz (g/mol)
P_1	61235	523	45261
P_2	65546	345	39186

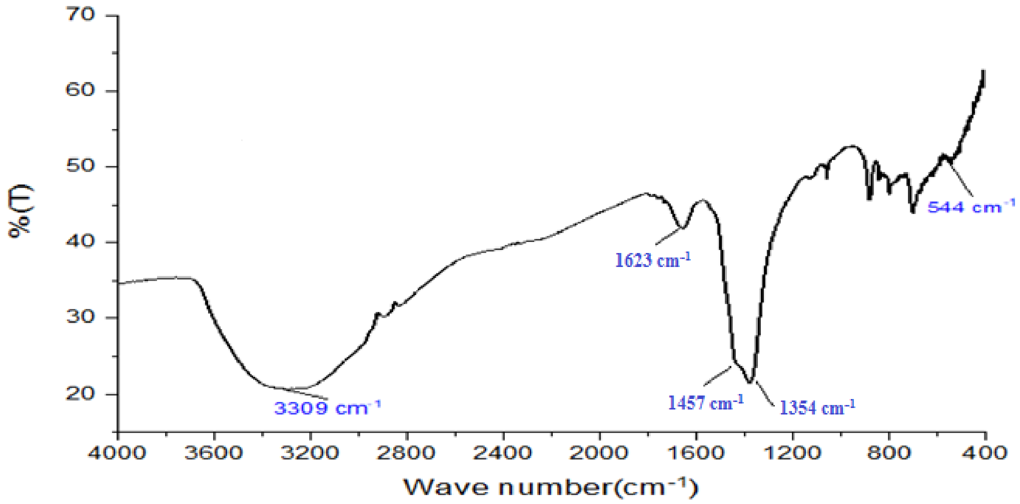

Fig. 9. FT-IR analysis of silver oxide nanoparticles (Ag_2O-NPs).

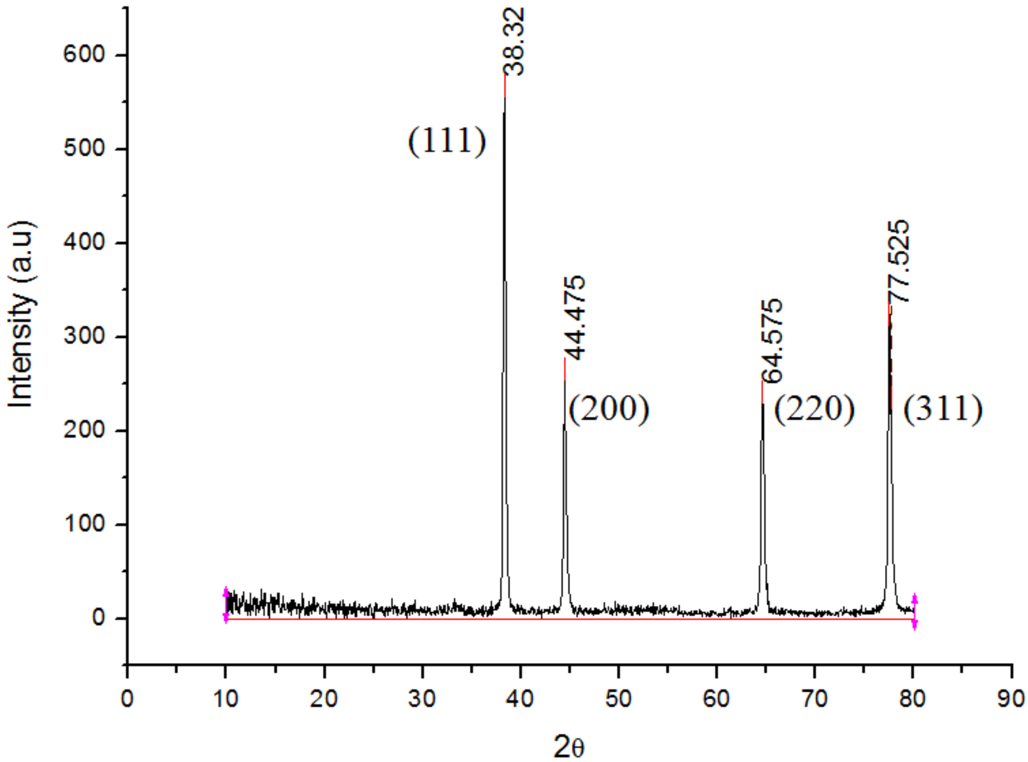

Fig. 10. X-ray diffraction pattern of silver oxide nanoparticles (Ag_2O NPs).

Table 4. XRD data of Ag_2O-NPs.

Pos. [°2Th.]	FWHM Left [°2Th.]	d-spacing [A°]	Height [cts]	Rel. Int. [%]	hkl	D,nm	δ	ε
38.3163	0.246	2.34915	561.43	100	111	35.72	0.000784	0.002146
44.4621	0.246	2.03767	260.33	46.37	200	36.45	0.000753	0.002145
64.5933	0.3444	1.44288	232.63	41.44	220	28.52	0.001229	0.003001
77.4962	0.1968	1.23173	318.44	56.72	311	54.09	0.000342	0.001713

to approximately 1650 cm^{-1} should belong to the stretching vibrations of C=C or the O–H bending mode. From FTIR results, it can be concluded that some of the bioorganic compounds from orange leaves extract formed the strong coating or capping on the Ag_2O-NPs.

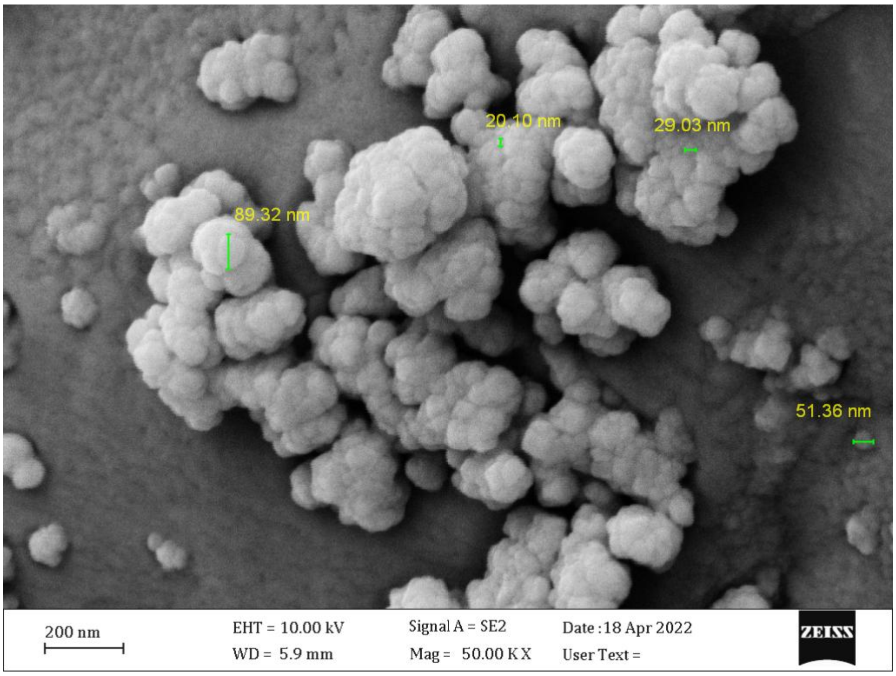

Fig. 11. FE-SEM image of silver oxide nanoparticles (Ag_2O-NPs).

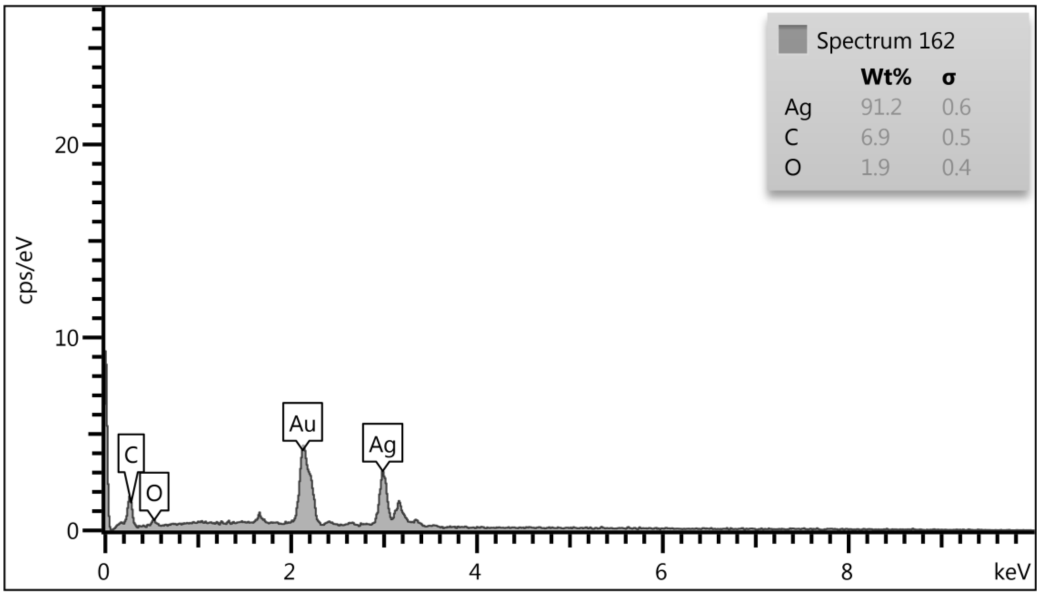

Fig. 12. Energy-dispersive X-ray (EDX) spectroscopy of synthesized silver oxide nanoparticles (Ag_2O-NPs).

XRD analysis

Fig. 10 shows the XRD pattern of Ag_2O-NPs synthesized by the green method. All the diffraction peaks of (111), (200), (220), and (311) can be well matched with the cubic phase structure with pattern peaks in T able 4. The structure of the resultant data is well matched with the JCPDS card number 03-0921[16]. The average crystallite size was calculated using the Debye–Scherrer equation and was found to be 38.69 nm. Expansive and sharp peaks were observed, which indicates the crystallite size and purity of Ag_2O-NPs [17].

The microstrain (ε) and dislocation density (δ) of Ag_2O- NPs was evaluated by using the respective formula [18]. The microstrain and dislocation density (lines/m2) values are reported in Table 4.

FE-SEM images of the silver oxide nanoparticles

The FE-SEM images of the silver oxide

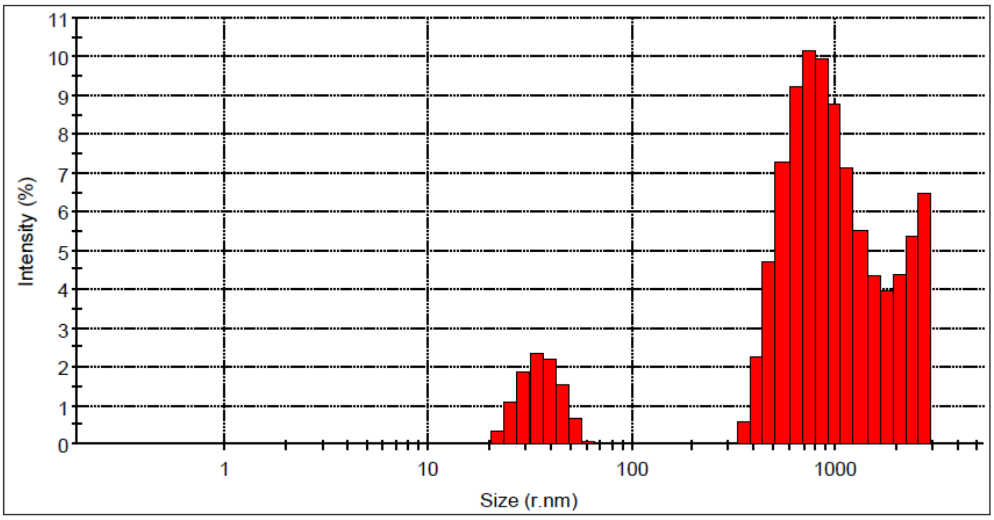

Fig. 13. DLS analysis of silver oxide nanoparticles (Ag_2O-NPs).

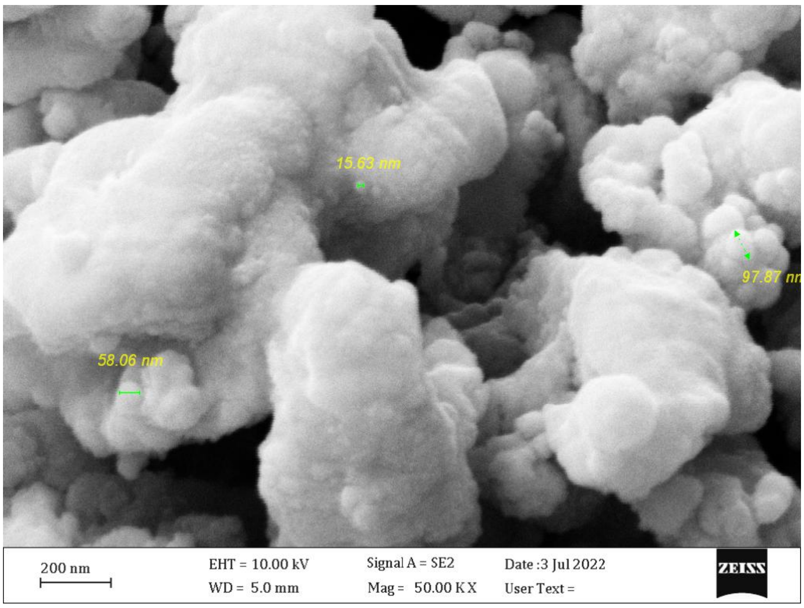

Fig. 14. FE-SEM image of Ag_2O/P_1 matrix.

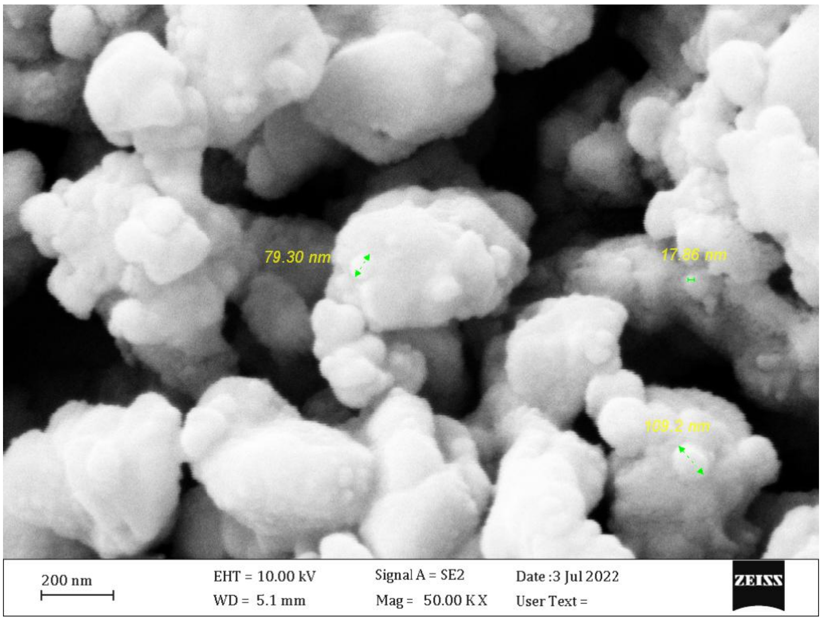

Fig. 15. FE-SEM image of Ag_2O/P_2 matrix.

nanoparticles are shown in Fig. 11. The surface morphology of silver oxide nanoparticles showed a shape and spherical nature agglomerated with average size about 47.45 nm, this value was further supported from the calculations made on the XRD pattern [19].

Energy-dispersive X-ray (EDX) study

Fig. 12 shows the energy dispersive spectrum of the synthesized silver nanoparticles, which suggests the presence of silver as the ingredient element. Silver nanoparticles generally show a typically signal peak at 3 keV, due to surface plasmon resonance. Fig. 12 shows the quantitative information of biosynthesized Ag_2O-NPs. The presence of elements such as Ag, O and C are shown in the inset of Fig. 12.

DLS analysis

The dynamic light scattering (DLS) data for Ag_2O-NPs displayed distribution in two peaks as a Fig. 13. It is observed that the size distribution of Ag_2O-NPs ranges from 30 to 70 nm and 450 to 1200 nm. The increase in the mean particle size can also be attributed to the agglomeration of smaller particles [20].

FE-SEM images of Ag_2O-NPs / polymer matrices

The FE-SEM images of the Ag_2O-NPs/ polymer matrices are shown in Figs. 14 and 15. The FE-SEM images, shows that the average size are 57.18 nm and 68.78 nm for the Ag_2O-NPs /P_1 and Ag_2O –NPs/P_2 matrices, respectively with few increase in the size of nanoparticles compare with Ag_2O-NPs image (Fig. 11) , and it shows that the Ag_2O- NPs are in spherical shape in the both cases.

CONCLUSION

In this study, novel copolymers were synthesized and Ag_2O nanoparticles was successfully synthesized achieved using the aqueous extract of the orange leaves extract. The process is easy, fast, cheap, environmentally friendly, and does not require any organic solvent or surfactant. Therefore, this synthesis method is more advantageous than traditional methods for the synthesis of Ag_2O nanoparticles. Ag_2O / polymer matrix were prepared from Ag_2O nanoparticles and polymers (P_1 and P_2) by chemical solution method were successful. The Ag_2O nanoparticles and their matrices Ag_2O / P1 and Ag_2O /P_2 matrix were almost spherical, of cubic crystalline nature, and the average crystal sizes are 47.45nm, 57.18nm, and 68.78nm respectively.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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